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EQUILIBRIUM COMPOSITIONS AND COMPRESSIBILITY FACTORS FOR AIR IN THE TEMPERATURE RANGE 1500 TO 13000 KELVIN AND FOR DENSITIES FROM 10^{-6} TO 10^{3} TIMES STANDARD DENSITY

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A formalism for computing thermodynamic properties and equilibrium compositions of reacting gas mixtures at high densities is developed. This formalism makes use of the Haar-Shenker version of the augmented hard sphere equation of state. The formalism is used for computing compressibility factors and equilibrium compositions of air in the temperature range 2,000 K - 13,000 K for densities from that appropriate to air at standard conditions (0°C, 1 atmosphere)

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20. ABSTRACT (Continued)

to densities 1000 times as great. These tables are consistent with the earlier NBS tables which covered the range up to 100 times that density. Some interesting features of the dependence of composition on density are discussed.

AFSC
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PREFACE

This research was conducted by the National Bureau of Standards (NBS), Heat Division, basically under sponsorship of the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Air Force Contract F40600-72-M-0002. The AEDC project monitor for this work was Elton R. Thompson, AEDC/DYR. The work was also supported in part by the Atomic Energy Commission under Interagency Agreement AT(49-16)3003, Modification No. 2. This work covers essentially the period July 1974 to June 1975. Principal investigators and authors of this report were Max Klein and Lester Haar of NBS.

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I. INTRODUCTION

Aerodynamic design requirements demand the ability to calculate tables of thermodynamic properties and equilibrium compositions of air for thermodynamic states far from normal laboratory conditions. Earlier design requirements led to the production of tables at very high temperatures ranging in density from quite low densities to intermediate densities. The NBS tables[1] (which were published under AEDC support) are examples of a response to this earlier need. These tables covered the temperature range 1500 K $\leq$ T $\leq$ 15,000 K and the density range $10^{-6} \leq \rho/\rho_o \leq 10^2$, where ρ_o is the density at the standard conditions of T = 273.15 K and P = 1 bar. More recently, there have been indications[2] of needs for tables covering considerably higher densities at these elevated temperatures.

In this project, we were requested to attempt to develop methods for the calculation of the properties of air for densities up to 1000 times normal sea level density. If successful, these tables, taken together with the NBS tables already published, would result in tables being available for the enormous density range $10^{-6} \leq \rho/\rho_o \leq 10^3$ (i.e. nine orders of magnitude) at temperatures well outside those associated with laboratory experiments. Such tables would then represent an extrapolation from ordinary conditions of over two orders of magnitude in temperature and at the same time, an extrapolation of at least one order of magnitude in density from the earlier tables.

Combined extrapolations of such magnitudes in temperature and density pose very difficult problems. They must of necessity be based on fundamental properties of the systems under study, properties which might not vary over the range of the extrapolation. These properties must also be used in a framework of fundamental theoretical methods valid over the entire range of temperatures and densities of interest. In addition, specific numerical methods must be developed and computer programs produced for transforming these numerical methods into the actual calculation of tables. These numerical problems include the often difficult task of producing methods for the solution of sets of non-linear algebraic equations,[3] with such methods being required to produce solutions for a wide variety of values for the unknown parameters.

It should be obvious that, because of the extent of the extrapolations required, empirical correlation methods are not appropriate here. Such engineering methods involve the least squares fitting of measured data to equations containing arbitrary parameters. Such parameters generally do not have physical significance and can therefore only be used with extreme caution if at all in extrapolations beyond the range of experimental data on which their values are based. In fact, using arbitrary parameters obtained by least squares fitting, in such long extrapolations beyond the range of their data base generally produces highly erratic behavior. Furthermore, considerable additional difficulty could be anticipated in applying such methods to mixtures. Mixing rules for non-physical parameters in the context of empirical correlations are generally arbitrary and often not useful even within the range of the data base and hence their behavior in extrapolations is unpredictable.

The original plan on which this research was based envisioned the use of the then developing and fundamentally based integral equation theory for the equation of state of fluids.[4] At the time this work began, that theory, though very promising for one component systems, had not been applied to mixtures nor had any attempt been made to integrate it into the context of chemical or phase equilibrium. It was not clear how one might calculate the free energy and chemical potentials of a multicomponent mixture within this approach. The study of the possibility of using the integral equation approach was, in fact, to constitute the major part of the research program supported by this contract with the probability of success not entirely clear. A rather complex and purely numerical approach was envisioned which, although it might of necessity be very complicated in a numerical sense, might nevertheless be expected ultimately to be made to work. Because of its expected complexity, the basic numerical parts of the problem were postponed in favor of a close study of the details of the integral equation approach itself. Initially, this involved examining integral equation methods as a means for representing the equation of state of pure substances before looking at them as possible methods for mixtures.

Any statistical mechanical method which could be used in this work (particularly one consistent with the earlier tables) including the integral equation approach, requires the use of intermolecular potential functions. For the temperatures of interest in aerodynamic problems, such intermolecular potential functions would certainly be used beyond the range in which data fits were carried out to obtain their parameters. This means that methods used to obtain these parameters would need to be understood very thoroughly. Furthermore, because of the implicit way in which the potential functions appear in statistical mechanical theories, the effect of uncertainties in their parameters on the accuracy of calculations in which they are used is not always clear. For these reasons, much of the time in this research program had to be spent in the study of the means by which intermolecular potential functions are obtained from experimental data of various kinds and in the study of the effect on calculated tables of extrapolating incorrect intermolecular functions[5]. Although this extrapolation of the potential parameters beyond the range of the data could be expected to introduce errors, these errors could be expected to be far less than those obtained from extrapolation of least squared fits to data such as are common in the usual empirical approaches. Furthermore, one might expect the general behavior of the functions calculated to be reasonable. This follows from the fact that the essential behavior of the potential function would be correct and from the fact that the "actual" potential functions would not vary with temperature so that the relationship between the potentials chosen and the "real" ones would not contain any hidden surprises on extrapolation to higher temperatures.

Although the present work emphasizes the high density region, it had to be designed to retain the earlier tables. Since these earlier calculations already covered densities up to 100 times normal sea level density, the extension from 100 to 1000 times normal density needed to be done using methods which included the earlier approach. At the highest densities, the earlier tables included a correction for the second virial coefficient based on the intermolecular forces between the molecules. Hence, almost any approach is consistent with the earlier tables if it makes use of a statistical mechanical theory based on these same intermolecular forces provided that this theory has the same (and correct) linear term in its low density expansion.

As the work progressed, alternative approaches were examined in an attempt to avoid the numerical complexity expected in the integral equation approach. These other methods were rejected either because their complexity did not offer any advantage over the integral equation approach or, more usually, because they required the extrapolation of parameters which had no physical basis. One alternative which appeared to hold promise, resulted from research by one of us (Lester Haar). An equation of state for single component fluids was developed which seemed to us capable of being used in this work in a computational procedure far simpler than that projected for the integral equation method. Also, it was based on fundamental ideas and was thought to provide a natural extension of the previous NBS tables. The approach is based on an equation of state due to Haar and Shenker[6], (HS), which was developed for the extrapolation of low density experimental data of one component system to high densities along isotherms at ordinary temperatures. According to the assumptions on which it was based, the HS equation was expected to work well at temperatures above the critical temperature and to improve with increasing temperature and this was indeed found to be the case by them. They also found indications that the method could be used to produce engineering calculations of reasonable accuracy even below the critical temperature into the liquid range.

The HS equation uses second virial coefficient data at each temperature as a basis for extrapolating to high densities. In our studies of the relationship between second virial coefficients and intermolecular potentials, we saw that the determination of intermolecular forces from second virial coefficients, if done properly, could be used to produce a temperature extrapolation of the second virial coeffcient to higher temperatures even as high as required in aerodynamic calculations. Thus, given an intermolecular potential function for a particular substance, a complete high temperature PVT surface could, in principle, be produced for that substance, with the potential function being used to calculate second virial coefficients at all temperatures of interest and these virial coefficients, in turn, serving as the basis for the HS equation at all densities.

Before it could be used in this work, the HS equation (which was developed for a pure substance) had to be extended to mixtures in the context of a reacting gas. This we have done and the details of the formalism will be presented in this report. The resulting formalism was used by us to produce the attached set of tables. A difficulty is expected to arise in this formalism whenever there is a need for intermolecular potential functions between fragments which are present in the mixture at high temperatures but which do not exist at ordinary temperatures. Potential functions between such molecular fragments can, however, often be characterized approximately by means of the potential function which describes the vibrational spectra of the combined fragments or, failing such spectra, from estimates of molecular sizes. Since estimates of the intermolecular forces between the various species had to be made for the earlier tables (including those species not present at ordinary temperatures), the basic data needed for this approach were actually already available at the start of this work. In order to ensure consistency in the initial calculations, we decided to use these same estimates of these forces in the calculations on which we report here.

Although the formal framework of the approach used by us is a valid one, the values contained in the attached tables should, for a number of reasons, only be considered an interim set of values:-

1. The estimates of the intermolecular potentials used are based on an old analysis by Woolley[7] in terms of the (12,6) potential function. As a result of our earlier work under AEDC support, better potentials are now known and should be used for the major species and these same potentials should also be used in place of the (12,6) for the new estimates of those associated with the minor species. As already mentioned, we used these older estimates so as to ensure consistency between these tables and the earlier tables.

2. In several cases, certain unknown intermolecular potential functions were arbitrarily taken as equivalent to others that were known. The effect of this could be important at the very highest densities.

3. As we shall describe below, we have used an ad hoc approach in the determination of hard sphere diameters at those temperatures for which the slope of the second virial coefficient is negative.

4. In this work only the compressibility factor and equilibrium compositions have been calculated.

Each of these compromises has been made in order to produce results to test the approach, leaving the production of more extensive tables for possible later work.

Grabau and Brahinsky[8], (GB), attempted an extrapolation of the earlier NBS tables to 10^3 times normal density for air and nitrogen. Their method was essentially semi-empirical. Their method was based on an equation having, in part, a fundamental basis and which contained a dependence on ideas partially related to the use of intermolecular forces. Their method could not be applied to a gas of varying composition (i.e. a reacting gas), for which reason they restricted their air calculations to temperatues below 6000K. Their method would also be expected to lose accuracy very rapidly at any temperature as the density increased due to a need for successive subtractions and because of their neglect of higher order terms. Since their method was based mainly on a graphical extrapolation, even qualitative estimates of its adequacy could not be made by them.

In this report, we compare our results with the extrapolation of Grabau and Brahinsky. These comparisons are interesting and will be discussed below. The agreement between the two extrapolations at intermediate density at the temperatures which they have in common is expected since the GB extrapolations were based on the earlier NBS tables with which our results are entirely consistent. The two results show considerable disagreement at the highest densities for reasons discussed below.

Our report contains plots at two representative temperatures of species concentrations for some important species. These plots show some interesting and possibly unexpected density behavior as discussed below. Information on composition behavior is not available in the approach of Grabau and Brahinsky since their method is applied to the thermodynamic properties only. Of particular interest in our plots are the dependences of concentrations on density as produced in three widely used approximations - the ideal gas, the second virial coefficient gas and the HS gas. Regardless of the ultimate accuracy of our own model, the differences among these three approximations can be expected to be indicative of the magnitude of the effect of the analogous three approximations in any other (and possibly more accurate) theoretical model.

Many unexpected technical numerical and computer programming problems were encountered in adding on the extreme high density end of the calculation. These had to do with numerical difficulties in obtaining solutions and will be discussed only in passing in this report.

II. THE EQUATION OF STATE OF HAAR AND SHENKER

A. BACKGROUND

The first step in the calculation of the thermodynamic properties of a reacting mixture involves the computation of the composition corresponding to reaction equilibrium. Within the framework of the formalism previously used by us, this corresponds to the solution of the equations associated with the law of mass action, as modified to take account of any non-ideal effects, subject to the conservation laws for nuclear types. The mass action relations can be written

$$C_i = \bar{K}_i(\rho/\rho_o)^{-\omega_i} \prod_{\ell} \gamma_i'^{(\ell)} \prod_{k} C_k^{\nu_{ik}} \tag{1}$$

where the C_k are the concentrations of the reference species, ν_{ik} the stoichiometric coefficients for the reaction, $\bar{K}_i = K_i(T/T_o)^{\omega_i}$ with K_i the equilibrium constant, $-\omega_i = \Sigma\nu_{ij}-1$ the net production of particles across the reaction, ρ_o the density at standard conditions (for P = one atmosphere pressure and for $T = T_o = 273.15$ kelvins) and where $\gamma_i'^{(\ell)}$ is the effective activity coefficient for the ℓ^{th} non-ideal effect for the i^{th} reaction. A detailed discussion of this equation and its derivation are contained in reference (3) and will not be repeated here. The γ_i' associated with the Debye-Huckel theory and that associated with the second virial coefficient are contained in Appendix B of reference (3). The derivation of the γ_i' for the HS equation constitutes a major part of this report. For the moment, it will be enough to state that, in principle, a γ_i' can be obtained for any equation of state but, in practice, the procedure is very complicated and not always clear. The understanding that formal expressions for the γ_i' for the HS equation can be obtained constitutes the motivation for the following extended discussion of that equation of state, of its development and of tests of its validity.

Haar and Shenker (HS), developed an extremely simple equation of state based on the virial expansion and on the behavior of the virial coefficients at high temperatures. The HS equation requires only a knowledge of the second virial coefficient and its first derivative at each temperature and from this the behavior at all densities is obtained. As already mentioned, the HS equation can be used, in a very simple and straightforward manner, to extrapolate PVT data in both the temperature and density directions. It is also expected to improve with increasing temperatures since the validity of the assumptions on which it is based improves with increasing temperature. It is therefore particularly well suited for these calculations.

The development of the equation of state was motivated by earlier work by Haar and Levelt Sengers[9] who showed that only two parameters are required to correlate thermodynamic properties for a number of simple non-polar gases along individual isotherms. The two parameters of Haar and Levelt Sengers had to be different for each temperature and were obtained by fits to experimental data on each isotherm. These two parameters could, in principle, be determined from experimental data at each temperature in a number of different ways.

The equation of state of Haar and Shenker also has two parameters for each isotherm with the values of the parameters being determined from values of the experimental second virial coefficient. Since there are two parameters at each temperature, two properties of the second virial coefficient are required at each temperature to determine their values. Haar and Shenker chose for these the second virial coefficient and its first derivative. The parameters so obtained can be regarded as being an effective temperature dependent molecular size, which sets the scale of density on the isotherm, and an effective temperature dependent molecular well depth which sets the temperature scale on which the isotherms are assigned. Each of these parameters is associated with the experimental system. In the following derivation these two quantities will be considered to be only slowly varying functions of the temperature which greatly simplifies their calculation. This assumption is certainly valid in the range of temperatures of interest in this work. In this way Haar and Shenker developed an equation of state for the correlation and prediction of high density data at temperatures above critical using two temperature dependent parameters. The parameters chosen have a fundamental basis and a simple method for their determination was devised. The fact that the parameters so chosen could also be associated with notions of corresponding states promised general success.

The repulsive energy between two molecules in a gas can generally be characterized by a very steep function at small intermolecular separations. To a first approximation this repulsion can be described by the interaction between hard spheres. Since repulsive effects are known to dominate at high temperatures[10], it is reasonable to take the equation of state of a gas of hard spheres (for which there are only repulsive effects) as a starting point in the development of an equation of state for any gas at high temperatures. To facilitate this, Haar and Shenker express the actual equation of state as the sum of a hard sphere contribution (to be calculated by a method as yet unspecified) plus the difference between the actual equation of state and this hard sphere contribution. This involves no approximations since the two parts add up identically to the actual equation of state regardless of how the hard sphere contribution is handled. The first approximating assumption consists in taking, for the hard sphere contribution, the result obtained from Percus-Yevick theory[11] using the compressibility equation of state. It has been shown that this representation differs only slightly from exact hard sphere theory up to densities approaching 2/3 the close packing density[12]. A second (and more serious) approximation involves the choice of method for obtaining the hard sphere diameters needed in the Percus-Yevick theory.

The derivation of the HS equation of state starts from the assumption that the N body potential of the fluid can be represented by a sum of pair-potentials and that the Ursell-Mayer virial expansion in the density[13] is valid for all potential functions of interest. The virial series for any potential is then transformed into a rapidly convergent expansion about the hard sphere series. Finally, the equation's parameters are fixed by imposing as boundary conditions the requirement that the first correction to the ideal gas be valid. This last follows automatically when the second virial coefficient is used to determine the parameters and is the basis of the consistency between our model and the earlier NBS tables.

B. DERIVATION FOR A PURE SUBSTANCE

The Ursell-Mayer expansion for the equation of state is written,

$$Z = \sum_{n=1}^{\infty} B_n \rho^{n-1} \quad , \tag{2}$$

where Z is the compressibility factor, defined by $Z = \frac{P\beta}{\rho N}$; ρ the reciprocal volume, P the pressure, $\beta = 1/kT$, and N the number of molecules in the system. The density expansion (2) for the compressibility factor is certainly valid in the gas phase and can be considered to be an exact representation of the compressibility factor Z. The B_n in (2) are the virial coefficients and are well-known[14] integrals, obtained from statistical mechanics, involving the intermolecular interactions among 2,3,4, etc. molecules respectively. We now formally develop each of these virials about that for a hard sphere of some (as yet arbitrary) diameter via the identity

$$B_n \equiv B_n^{h.s.} + B_n - B_n^{h.s.} \quad , \tag{3}$$

where $B_n^{h.s.}$ is the nth virial coefficient for the hard sphere. Using (3), we can rewrite eq. (2)

$$Z = \sum_{n=1}^{\infty} B_n^{h.s.} \rho^{n-1} + \sum_{n=1}^{\infty} (B_n - B_n^{h.s.}) \rho^{n-1} \quad , \tag{4}$$

where, consistent with the formulation, $B_1^{h.s.} = B_1 = 1$. It should be noted that (4) is an identity and so does not involve any new assumptions. (4) is therefore still an exact representation for Z. The first sum on the right-hand side of Eq. (4) is the equation of state that would be obtained for a gas made up of identical hard sphere molecules. The hard-sphere gas has been studied extensively in computer "experiments" via molecular dynamics[15] and Monte Carlo[16] calculations and theoretically via the Percus-Yevick approximation. The hard-sphere summation in (4) can therefore be considered to be known for any particular sphere size. The task inherent in the evaluation of (4) is to obtain a simple representation for the perturbation terms, i.e. the second sum on the right of Eq. (4), and to obtain a proper hard sphere diameter to use in the first term.

We now present an argument which shows that the perturbation terms, i.e. the second sum on the right-hand side of (4), converge rapidly above the gas-liquid critical temperature so that at such temperatures only the term linear in density needs to be considered. The prospect that this convergence might persist to somewhat lower temperatures is implied in work by Woolley[17].

To illustrate our argument, in Fig. 1 we plot a few of the lower virial coefficients for the Lennard-Jones (12,6) pair-potential. The reduced virials B_2^*, B_3^*, and B_4^* with

$$B_n^* = B_n/[\tfrac{2}{3}\pi N \sigma^3]^{n-1},$$

are plotted against the reduced temperature $T^* = (\beta\epsilon)^{-1}$, where σ is the Lennard-Jones length parameter and ϵ the well depth. At low temperatures the contribution from the attractive part of the potential (regions of negative energy) is important and the lower virials tend to large negative values. At the higher temperatures, the repulsive part of the potential (regions of positive energy) tends to yield the dominant contribution and the virials become positive. Thus, in Fig. 1 we see that B_2^* monotonically increases, with decreasing slope, from large negative values to positive ones, finally passing through a maximum. It is apparent that as the temperature increases, the contribution of attraction decreases relative to that of repulsion, even though the contribution of repulsion is itself slowly decreasing with increasing temperature. We suggest that at some temperature, not much beyond the temperature where B_2^* achieves its maximum, the contribution of attraction to B_2^* is relatively small. This occurs at a reduced temperature somewhat above $T^* = 30$. Thus if the hard-sphere contribution is chosen appropriately, we would expect that the perturbation terms linear in density would be quite small at temperatures somewhat above $T^* = 30$. Likewise we expect that for the third, fourth, etc. virials the contribution of attraction becomes relatively small at temperatures starting somewhat above the temperatures for which these virial coefficients achieve their (initial) maxima. The maximum for the third virial coefficient occurs at about $T^* = 1.25$ corresponding to a temperature near the liquid-vapor critical point for simple substances. The temperature at which the fourth virial coefficient would achieve its maximum is also in this neighborhood. (This is also true for the fifth virial coefficient not shown in the figure[18]).We invoke a corresponding states argument and assume that the disappearance of attractive contributions to the third and higher virial coefficients above the critical temperature should be a general property of any simple gas. Thus, we suggest that at temperatures somewhat above the critical temperature the second virial coefficient includes all of the major effects due to molecular attractions, and that the higher virial coefficients are primarily determined by the repulsive interaction. For each substance, at any given temperature, we therefore represent the repulsion between the molecules by that in a gas made up of identical hard spheres whose diameter is somehow chosen so as to be appropriate to that substance at that temperature. We then use this hard sphere gas to represent the total contribution of each of the virials above the second at that temperature. This certainly should be a good model at the temperatures of interest in our work.

Based on the preceding arguments, for temperatures of interest here, the second sum in the equation of state, Eq. (4), can be truncated after the term linear in the attractive contribution. The hard sphere part, on the other hand, contains contributions to all orders of the density. To represent this hard sphere part, we employ the results of the Percus-Yevick theory[11] using the compressibility form for the equation of state. This is a good approximation at low densities, and is in error by, at most, 5% at densities approaching 2/3 close packing of hard spheres, a density well beyond those of interest here. The equation of state is written, therefore,

$$Z \simeq \frac{1 + y + y^2}{(1-y)^3} + 4y\left(\frac{B_2}{b} - 1\right), \qquad (5)$$

where $4y = b\rho$, and b is the hard sphere second virial coefficient,

$$b = \frac{2}{3} \pi N a^3 \qquad (6)$$

a being the temperature dependent hard sphere diameter. For a given temperature Eq. (5) is a two constant equation of state, these constants being the hard sphere diameter a and the well depth associated with the representation of B_2. An important feature to be used below is that the equation (5) is easily integrable in closed form to yield a free energy.

As already mentioned, to evaluate the two equation of state parameters for a particular gas at each temperature we shall employ the numerical values, for that gas, of the second virial coefficient and its first temperature derivative. To bring out the connection between these two parameters and the molecular diameter and the intermolecular well depth, we introduce an effective intermolecular interaction that has the general features of a typical pair potential, except that it is specifically characterized by a hard sphere cut-off at some diameter a(T) at which point it is joined to an attractive bowl of well depth $\varepsilon(T)$ (Note that we have explicitly indicated the temperature dependence of these quantities.) The purpose of this effective function is to provide a means for transforming the repulsive and attractive parts of the "actual" potential of the gas into an explicit hard sphere diameter and a well depth. Typical functions of this kind are shown in Fig. 2.

A simple numerical method has been developed for the determination of the parameters a and ε at each temperature. The method starts with tables of reduced second virial coefficients B^* and their first derivative $T^* \frac{dB^*}{dT^*}$ for the effective potential function (i.e. the function with the hard sphere cut-off). At any given temperature, these reduced quantities are required to yield the values associated with the experimental system being described. Thus the conditions on these reduced quantities are,

$$B_{exp}(T) = b\, B^*(kT/\varepsilon) \qquad (7)$$

and

$$T \frac{dB_{exp}(T)}{dT} = b\, T^* \frac{dB^*}{dT^*} (kT/\varepsilon) \qquad (8)$$

where T is the temperature of interest. On the right-hand side, we have indicated the dependence on T^* by kT/ε to emphasize the fact that ε/k is an unknown quantity. The right-hand sides in (7) and (8) are the reduced quantities as calculated for the effective potential function (i.e. the potential with the hard core). It should be noted that the right hand side of equation (8) contains the implicit assumptions that $\frac{da}{dT}$ and $d\varepsilon/dT$ can be neglected in the calculation of a and ε. On dividing Eq. (8) by Eq. (7), there results

$$\frac{T}{B_{exp}} \frac{dB_{exp}}{dT} = \frac{T^*}{B^*} \frac{dB^*}{dT^*} = Q^* \qquad (9)$$

It is a simple matter to produce a table of values for the quantity Q^* as a function of T^* for the effective potential function. By way of illustration Q^* values are listed in Table 1 for a particular effective potential. The same quantity (i.e. the left hand side of (9)) is then calculated from experimental data as a function of T. (9) is then solved for ε/k at a given experimental temperature T. This is done by starting with the experimental value of Q^* at that value of T, and, by interpolation, finding that value of Q^* and the value of T^* associated with it in the table of values calculated for the effective potential. ε/k is then calculated at that temperature from the relation

$$\varepsilon/k = T/T^*$$

This procedure guarantees that Eq. (9) is automatically satisfied at the chosen experimental value of T. This ε/k value is then used in (7) to obtain b and therefore a^3. By carrying out this procedure at each temperature, a(T) and ε(T) are determined for all experimental points. The equation of state is then calculated at each temperature T using b(T) and $B_2^*(T^*)$ in equation (5). (The use of $B_2^*(T^*)$ is equivalent to the use of ε(T)).

One of the difficulties associated with the above procedure involves the calculation of dB/dT from experimental data which are generally not smooth and not presented at convenient temperature intervals. A reasonable way to do this is first to fit the experimental B(T) data to a realistic (i.e. one which contains a dependence on r for small r) potential function (as opposed to the effective potential which has a hard core cut-off for small r) and to calculate smooth tables of B_{exp} and $\frac{dB_{exp}}{dT}$ values using that function.

The procedure outlined for solving Eq. (9) does not work for those temperature at which $dB_{exp}/dT < 0$. Because the effective potential has a hard core repulsion, its second virial coefficient does not have a region of negative slope and solution of (9) becomes impossible since the negative value of Q^* associated with the experimental system is being sought in the table for the effective potential which contains only positive values. Under such conditions, we have proceeded by neglecting the attractive contribution by setting B^* equal to unity in (7). This leads to a negligible discontinuity in b(T) but in a non-negligible one in its temperature derivative.

C. COMPARISONS WITH EXPERIMENTAL DATA AND OTHER THEORIES

1. Sensitivity to the selection of the attractive part of the effective potential.

It should be obvious that the effective potential plays no fundamental role in the HS theory but is used only for computational convenience, being used to extract an effective hard sphere diameter from the second virial coefficient. It clearly should not be allowed to introduce any of its own character into the calculation. For this reason, we shall precede a detailed comparison with experiment, by an examination of the sensitivity of our method to any particular choice for the shape of the bowl used in the effective potential. In Fig. 3 a plot of the sphere diameter a(T) vs. T^* is shown for the two effective potential functions corresponding to m=9 and m=10. As expected from the behavior of a typical intermolecular potential function at small separation, the effective sphere diameter is a monotonically decreasing function of the temperature. The scale of the abscissa is normalized so that a(T) = 1 for the effective potential function given by m=12. The parameters a and ε were calculated from equations (7) and (9) for each of these effective potentials using values for B_2 and dB_2/dT

calculated with a Lennard-Jones (12,6) potential in place of experimental data. The choice of a particular effective potential function, that is, the choice for the shape of the potential bowl in Figure 2, is far from unique, for, in addition to the dependence on m, the bowl shape could be affected by adjusting the exponent in the attractive term.

At a reduced temperature $T^* = 3.0$, a(T), and hence the equation of state, was found to be relatively insensitive to m, that is, to the shape of the bowl appended to the hard sphere core. At higher temperatures, the sphere diameter becomes completely independent of m. In such a case, the procedure used for the evaluation of the sphere size can be further simplified, as will be discussed below. On the other hand, as the temperature is reduced, the hard-sphere size tends to become increasingly sensitive to m. This results in a useful procedure for determining an optimum value for m for a given substance. This consists of comparing experimental PVT data with those predicted by the HS equation at a low temperature for effective potentials characterized by several values of m until a best fit is obtained. Because of the insensitivity to m already described, the value of m chosen can obviously be used at higher temperatures. The method has thus been modified to produce a good low temperature fit. Haar and Shenker used an isotherm near 3/2 times the critical temperature for the low temperature fitting.

We include, in the next section, a comparison of the predictions of the HS equation with other theories and with experimental data for argon and nitrogen. It is easily determined that m=9 and m=10, respectively, are reasonable values of m for these fluids. Since the sensitivity of the equation of state properties to m is weak except at low temperatures, m=9 can also be taken for nitrogen when the temperatures of interest do not extend much below twice the critical.

2. Relationship to other fundamental equations of state.

It is useful to compare the HS equation with equations of state which have the appearance of being more fundamentally based. The latter are invariably much more complicated than is the HS equation so would have to produce far superior results to it to warrant their choice over it. In this comparison, we shall include an example of an integral equation (the Percus-Yevick) as well as the perturbation theory approach of Barker and Henderson. Although the latter is developed totally within the language of statistical mechanics, it is not unrelated to the Haar-Shenker approach which has been described with an emphasis on phenomenological language.

A major objective of statistical mechanics is to predict the properties for real fluids at high densities from the known properties of the dilute gas. To accomplish this, it is usual practice to reduce exact theories (such as that associated with Eq. (2)) to theories in which interactions among several particles are pairwise additive. The properties of the dense fluid can then be formulated in terms of the detailed structure of the potential functions which describe the forces between pairs of particles. Considerable progress has been realized using this approach. Relevant to our work are the expansions in density based on Percus-Yevick (PY) theory and expansions in reciprocal temperature using the Zwanzig theory[19] as modified by Barker and Henderson[20] (ZBH). These have been tried for several potential models including the hard and soft spheres, the square well, and the Lennard-Jones potential. The ZBH temperature perturbation theory appears to be the more successful when compared to results of computer experiments, particularly at liquid temperatures but also for gases at high densities and at high temperatures.

Though the ZBH theory is a physically satisfying approach and does compare well (except at low liquid temperatures) with results of "computer experiments", we note several practical limitations. The most serious of these is associated with the application of the theory to real fluids. In the ZBH theory the perturbation terms are obtained as an expansion about the hard sphere. Barker and Henderson have shown[20] that the theory can yield quantitative results when the sphere diameter is expressed in terms of a kind of Boltzmann average of the molecular separation, where the average is taken over the positive energy region of the pair potential. Sphere sizes calculated in this way are also contained in Figure 3. It is a fact, however, that the shape of the pair potential even for simple systems is quite uncertain. In this connection it has been proven[21] that for realistic (non-monotone) potentials it is not possible to obtain an unambiguous representation of the pair potential from second virial coefficients. Also at high densities the sphere volume tends to affect the equation of state properties somewhat like an excluded volume, so that ambiguities in the sphere diameter are amplified in their effect on the equation of state at high densities. We shall present an example of this below. Thus, though the ZBH theory is theoretically satisfying, its application would seem to be limited to situations where the pair potential is known, as is the case for "computer experiments". The fact that the use of this equation of state to produce thermodynamic tables requires a complicated numerical integration poses a second limitation to the ZBH approach. Because of this, results have so far been obtained as a theoretical end in themselves and are therefore of somewhat limited utility to the engineer or scientist who desires a simple analytic representation of the equation of state as a predictive tool.

It should be appreciated that the hard-sphere diameters are only convenient artifices. Physical interpretation is meaningful only in the context of the particular overall theory. However, since the ZBH and the present theory are quite sensitive to the hard-sphere diameter, agreement between them at least to within several percent for a(T) would be necessary for the two approaches to yield comparable equation of state properties at high densities.

3. Comparisons of the HS equation of state with experiment and with other theories.

In this section the HS equation of state is used to calculate compressibility factors for the real fluids argon and molecular nitrogen. The results are compared with PVT experimental data, and, in the case of argon, with results of "computer experiments" and with ZBH theory. The experimental second virial coefficients used as input data to obtain the required parameters are smoothed values calculated from model pair potentials as determined from the experimental second virials.

The Figs. 4-8 contain isotherms calculated for argon using the HS equation of state and the ZBH theory. The compressibility factor is plotted versus the reduced density, $\rho^* = N\sigma^3\rho$, for isotherms from 119.8K (≈.8 critical) to 673.15K. Curves labeled #1 represent the compressibility factors predicted by the HS equation of state. The curves #2, #3 and #4 represent results of second order temperature perturbation ZBH theory, for a Lennard-Jones gas with parameters ε/k = 119.8K and σ = 3.405 Å as reported in references 22, 23 and 24, respectively: the curves #2 and #4 are obtained by numerical integration of approximate expressions for the perturbation terms and are essentially equivalent treatments; the curves #3 refer to an "exact" calculation of the second order perturbation terms via Monte Carlo techniques. The curves #5 represent experimental compressibility factors measured for argon. The data points on Figs. 4, 5 and 6 are results of "computer experiments" for the Lennard-Jones gas with the above parameters, the circled points referring to Monte Carlo results and the boxed points to molecular dynamics results. The "computer experiments" could be uncertain by 5 to 10%.

Since use of the Lennard-Jones potential with the above parameters does not produce second virial coefficients which fit the data for argon below 200K[25], Figs. 4-6 are interesting primarily as comparisons of theory with the results of the "computer experiments." These figures show that the present theory, as well as the ZBH theory, are only qualitative at these temperatures. However, the ZBH curves #3 yield a somewhat closer approximation to the results of "computer experiments" for liquid densities. As previously stated, the Haar-Shenker equation of state tends to degrade at low temperatures. But it is apparent from Fig. 4 that the theory is still at least qualitatively good at temperatures even as low as .8 of the critical temperature. In fact it is only for curves #3 (which involve extensive numerical calculations to evaluate the second order perturbation terms) that the temperature perturbation results are a significant improvement over the HS equation of state.

An explanation for the fact that the "wrong" potential gives the correct results in the ZBH theory for argon has been offered by Barker, Henderson and Smith.[26] They argue, that the (12,6) pair-potential with the above parameters happens to be an "effective potential" that, to first order for argon, accounts for high density non-additive effects.

The Figs. 6-8 include the temperature region for which the pair potential used produces a good fit to the experimental second virial data. Comparisons of our results with experimental PVT measurements for these temperatures are therefore more meaningful. The HS equation of state (curves #1) tends to follow the PVT experimental data (curves #5) fairly closely at the lower densities, up to about $\rho^* = 0.6$ (which is approximately twice the critical density). At higher densities it tends to yield values that are low, but in most cases only by less than 5%. The results are roughly comparable to those for the more complicated ZBH theory. The ZBH theory (curves #2, #3, #4,), however, tends to underestimate at densities near the critical and to overestimate at high densities. The results of the "computer experiments" seem to scatter among the various theories. Thus, in Fig. 6. at $\rho^* = .75$, the Monte Carlo results tend to favor the HS theory, at $\rho^* = .9$, they favor the ZBH; while at $\rho^* = 0.55$ they fall between the results of the two theories, in fact, almost on the PVT experimental curve #5.

We have stated above that uncertainties in the pair potential for real fluids limit the utility of the ZBH theory as a tool for predicting the equation of state properties for such fluids. To illustrate this we compare the equation of state of argon for a particular isotherm with the ZBH and HS theories, in which different inverse power representations for the pair potential are used, each of which produces an equivalent fit to the experimental second virials.[27] In Figs. 10 and 11 equation of state results are presented for two representations for the pair potential for argon: the (18,6) with the parameters[25]

$$\varepsilon/k = 160.87 \text{ K}$$
$$\sigma = 3.261 \text{ Å} .$$

as curves #1; the (12,6) with parameters given earlier, curves #2. Fig. 10 includes the results for the ZBH theory; Fig.11 those of the HS equation. Both figures refer to the isotherm 239.8K. In these figures the compressibility factor is plotted against the density in amagats. All the numerical data for Fig.10 were furnished by Toxvaerd.[23] The results for Fig.10 show the two curves near coincidence up to a density about 2/3 the critical (critical density for argon $\cong$ 300 amagats) but sharply divergent at higher densities. By comparison, the results for the HS theory in Fig.11 are relatively potential independent. The reason for this independence is obvious. The HS equation depends only on the experimental second virial coefficient and its first derivative. Since the same values for the second virial coefficient are obtained for either potential for a range of temperatures near this one ($T^*_{12,6} = 2.0$), the calculated second virials and their first derivatives are equivalent. Since the details of the repulsive branches of the potentials are different, however, the calculation of the hard sphere diameter according to the prescription of Barker and Henderson yields different results for the two potentials. This difference, in turn, produces a difference in the equation of state predicted.

Finally, in Figs. 12-15 we present results of using the HS theory for calculating the equation of state of molecular nitrogen. The compressibility factor is plotted versus the fluid density in amagat units. Here, the experimental second virial coefficients were represented by smoothed tables calculated using the Lennard-Jones pair potential with parameters ε/k = 95.781K, and σ = 3.712 Å. The curves #1 refer to the present theory; the curves #2 to experimental PVT measurements. The latter extend to 10,000 atm in Fig. 15. The sphere diameters are obtained from Fig. 3 with m=10. The comparison of theory with experiment for nitrogen is quite similar to that for argon. As with argon, the HS theory is in good agreement with experiment at low densities, but at the higher densities the experimental PVT isotherms tend to be slightly steeper.

4. Summary.

Based on the virial expansion and on the behavior of the virial coefficients at high temperature, Haar and Shenker derived a quantitative yet simple equation of state which is valid for real fluids over a density range from the dilute gas to densities approaching that of the solid at temperatures above twice critical, and which requires only a knowledge of the second virial coefficient and its first derivative at each temperature. This equation of state is much simpler than the ZBH temperature perturbation theory and furthermore does not require reference to the precise details of the pair potentials. The equation proved to be quite successful in comparisons with experimental data. These comparisons were naturally carried out for ordinary temperatures since experimental data exist only for such temperatures. Figures 2 and 3 contain such comparisons for argon and nitrogen.

Through the use of the intermolecular potential function, the HS equation of state can be used, in a very simple and straightforward manner, to extrapolate PVT data in both the temperature and density directions. Thus, the intermolecular potential is used to extrapolate the second virial coefficient as a function of temperature and this, in turn, is used with the HS equation to cover all fluid densities. This approach is therefore particularly well suited for aerodynamic calculations since, as already mentioned, these require temperature extrapolations of up to a factor of ten for densities up to those which, at low temperatures, correspond to the liquid. Because of the decrease in the attractive contribution to the second virial coefficient with temperature, this equation of state should improve with increasing temperature. As a result, the comparisons made at ordinary temperatures should easily be sufficient for estimating the expected adequacy of the theory at high temperatures. Since this equation of state depends only on the second virial coefficient which, in turn, is determined once the intermolecular potential is known, it becomes possible to develop an entire PVT surface given this intermolecular potential function, or equivalently, given a sufficient (generally small) amount of low density PVT data for the substance at ordinary temperatures, from which data the intermolecular potential can be obtained.

The derivation of the equation of state is based on an expansion in density, where the reference state is a gas of hard spheres. We have presented a plausibility argument which indicates that, when the sphere diameter is chosen appropriately, the terms that account for the differences between the properties of the actual fluid and those calculated for a fluid of hard spheres are sharply attenuated at temperatures above the liquid-vapor critical temperature, for densities up to that of the solid.

It has been shown that the temperature dependence of the equation of state at temperatures above the critical is determined by two parameters which depend on temperature and that these parameters can be obtained from the second virial coefficient and its first temperature derivative.

III. THE EXTENSION OF THE HAAR-SHENKER EQUATION OF STATE TO MIXTURES

Haar and Shenker developed their equation of state for use with pure substances. Our needs are, of course, for a theory applicable to mixtures since at aerodynamic temperatures even pure nitrogen becomes a mixture as a result of dissociation and ionization. There are several ways in which a theory for pure fluids can be extended to mixtures. Perhaps the simplest are what have been called the one and two fluid van der Waals' theories. In the one fluid model the mixture behaves as if it were a single component fluid (which can be called the equivalent fluid) with any parameters used to describe the fluid being averaged over the composition. This averaging is carried out by taking the parameters associated with the individual constituents and suitably weighting them to the extent that the constituents are present in the fluid. For example, a fluid made up of a mixture of hard spheres would be described as a one fluid van der Waals' model by the equations associated with a single component hard sphere fluid but with the single relevant parameter (that associated with the molecular diameter) averaged over the composition. A natural way of doing this is to take for the hard sphere volume

$$\sigma_{eq}^3 = \sum_{i,j} X_i X_j \sigma_{ij}^3$$

where σ_{eq} is the diameter of the molecules of the equivalent fluid and σ_{ij} the diameter for the interaction between a molecule of the i^{th} species and one of the j^{th} species in the actual fluid. For hard spheres $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$.

The equation of state for this mixture is easily derived. From the virial theorem, it is possible to derive a general equation of state for a fluid in terms of the distribution of pairs of particles in the fluid.[28] Because of the abruptness of the hard sphere interaction, this equation, for a one component hard sphere fluid, reduces to

$$\frac{PV}{RT} = 1 + \frac{2\pi}{3} \rho\sigma^3 g(\sigma) \qquad (10)$$

where $g(\sigma)$ is the probability that a pair of molecules will be found a distance σ apart. For a mixture of such spheres, the equation of state becomes

$$\frac{PV}{RT} = 1 + \frac{2\pi}{3} \rho \sum_{i,j} X_i X_j \sigma_{ij}^3 g_{ij} (\sigma_{ij}) \qquad (11)$$

where $g_{ij}(\sigma_{ij})$ is the probability that a pair of molecules, one of the i^{th} species and one of the j^{th} species, are separated by a distance σ_{ij}. In the one fluid model, then, (11) is replaced by (10) in which

$$g_{ij}(\sigma_{ij}) = g(\sigma)$$

and

$$\sigma^3 = \sum_{i,j} X_i X_j \sigma_{ij}^3 \tag{12}$$

This model is consistent with the results of the density expansion in the Ursell-Mayer virial equation of state.

A number of models other than (12) can be devised for using (10) in place of (11) for a mixture. Each of these, though reasonable, does not lead from (11) to (10) in a natural way. One might, for instance, average the diameter rather than the volume so that

$$\sigma = \sum_{i,j} X_i X_j \sigma_{ij} = \sum_i X_i \sigma_{ii} \text{ since } \sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$$

One might also average the volumes over like species only, i.e. $\sigma^3 = \sum_i X_i \sigma_{ii}^3$. We shall consider (12) as the only reasonable model, particularly since it is the only one that leads to results which are satisfactory.

A two fluid theory can be obtained from the approximation

$$g_{ij}(\sigma_{ij}) = \frac{1}{2}\left[g_{ii}(\sigma_{ii}) + g_{jj}(\sigma_{jj})\right]$$

If, at the same time, one uses the fact that, for hard spheres $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ (11) becomes, for this model,

$$\frac{PV}{RT} = 1 + \frac{2\pi}{3} \rho \sum_{i} X_i \, \sigma_i^3 \, g_{ii} \, (\sigma_{ii}) \tag{13}$$

In order for this to be of the pure fluid form, it must be assumed that g_{ii} is the distribution function for a pure fluid of hard spheres of volume σ_i^3 given by

$$\sigma_i^3 = \sum_{j} X_j \cdot \sigma_{ij}^3$$

Thus, if this were a binary system, it would appear to be made up of two pure fluids of different diameters, namely $\sigma_1^3 = X_1 \, \sigma_{11}^3 + X_2 \, \sigma_{12}^3$ and $\sigma_2^3 = X_1 \, \sigma_{21}^3 + X_2 \, \sigma_{22}^3$. Hence the name two fluid theory.

A fluid of hard spheres is a highly idealized model for an actual fluid so might be thought to be quite useless for testing theories of fluids. There are, however, properties for fluids of hard spheres as calculated by computer simulation methods. If such results obtained for hard sphere mixtures are taken as "experimental" data, it is then reasonable to compare them with (12) and (13) to see which is the better approximation to a mixture of hard spheres. This has been done by Henderson and Leonard[29] who found the one fluid theory to be, by far, the superior.

In a later paper, these same authors carried out a similar comparison[30] for a fluid whose molecules interact in accordance with a Lennard-Jones (12,6) potential function. Such a potential contains both attraction and repulsion, and is often characterized by a molecular diameter and by a potential well depth. The one fluid model now follows from $\varepsilon\sigma^3 = \sum_{i,j} X_i \, X_j \, \varepsilon_{ij} \, \sigma^3_{ij}$. Comparisons were made for an equimolar mixture and the one fluid model was found to be superior, particularly in the prediction of the excess free energy and heat of mixing. The intercomparison for the excess volume of mixing was somewhat ambiguous, however.

It would thus seem clear that the most reasonable way in which a theory for a pure fluid can be applied to that for a mixture is via a one fluid model. This we have chosen to do for the HS equation of state. This simplifies our task since we need only write down the pure fluid form of the equation of state which we have already derived and interpret the parameters in the form of the one fluid theory.

By (5), the HS equation of state for a pure fluid is written

$$\frac{PV}{RT} = \frac{1+y+y^2}{(1-y)^3} + 4\left(\frac{B}{b} - 1\right)y \qquad (14)$$

where $y = \frac{b\rho}{4}$. Then Eq. (14) becomes an equation of state for a mixture according to the one fluid model, if

$$b = \sum_{i,j} X_i X_j b_{ij} \qquad (15)$$

$$B = \sum_{i,j} X_i X_j B_{ij} \qquad (16)$$

It should be remembered that Eq. (9) must be solved for b_{ij} for each of the interactions included.

IV. THERMODYNAMIC FUNCTIONS IN THE ONE FLUID HS MODEL

In this section of the report we shall be concerned only with the real gas contributions to the various thermodynamic properties. The ideal gas contributions and certain precautions required in their calculation are contained in reference (3).

A. HELMHOLTZ FREE ENERGY, CHEMICAL POTENTIAL, AND ACTIVITY COEFFICIENTS.

The combination of the equation of state (14) and the one fluid model, (15) and (16), is sufficient for the calculation of the equation of state of a real gas mixture at high densities. With such an equation of state it then becomes possible to calculate the real gas part of the Helmholtz free energy from

$$A = -\int P dV$$

from which the chemical potential can be calculated using

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,\ \rho,\ \vec{n}_j} \qquad \text{when } \vec{n}_j \text{ refers to all } n_j,\ j \neq i.$$

When the ideal and real parts of the chemical potential are separated it becomes possible to identify the activity coefficient for each species. By properly combining the activity coefficients for each species taking part in a chemical reaction, one can define an effective activity coefficient for that chemical reaction. This effective activity coefficient directly modifies the equilibrium constant to produce the effect of non-ideality on the chemical reaction. To see how this goes, let

$$\mu_i = \mu_i^{(o)} + \Delta\,\mu_i$$

where $\mu_i^{(o)}$ is the ideal gas part of the chemical potential and $\Delta\mu_i$ the real part. It follows, then, that the activity coefficient γ_i for this species is given by

$$\frac{\Delta\mu_i}{RT} = \ln \gamma_i$$

The effective activity coefficient for species i in a chemical reaction with stoichiometric coefficients ν_{ij}, is then given by

$$\gamma_i^1 = [\prod_j \gamma_j^{\nu_{ij}}]/\gamma_i$$

which is equivalent to

$$\gamma_i^1 = \exp\,[(\sum_j \nu_{ij}\,\Delta\mu_j - \Delta\mu_i)/RT] \qquad (17)$$

We shall now proceed to the detailed calculation of the free energy and chemical potential for the HS equation of state.

If at each volume the reference state for the free energy is taken as that of the ideal gas at that volume then

$$A(V) = A(\infty) - \int_\infty^V P dV$$

$$A^{(o)}(V) = A^{(o)}(\infty) - \int_\infty^V P^{(o)}\, dV$$

But, since $A(\infty) = A^{(o)}(\infty)$ it follows that

$$A(V) - A^{(o)}(V) = - \int_\infty^V (P - P^{(o)})\, dV$$

Since $P = \frac{nZRT}{V}$ and $P^{(o)} = \frac{nRT}{V}$, where Z is the compressibility factor and n the total number of moles, it follows that

$$A(V) - A^{(o)}(V) = - nRT \int_\infty^V (Z-1)\, \frac{dV}{V}$$

The real part of the chemical potential is then given by

$$\frac{\Delta\mu_i}{RT} = \frac{\mu_i - \mu_i^{(o)}}{RT} = - \frac{\partial}{\partial n_i}\, n \int_{\infty}^{V} (Z-1)\, \frac{dV}{V}$$

The evaluation of the common integral is obviously necessary to progress in the derivation of both the free energy and the chemical potential.

According to the HS theory,

$$(Z-1) = \frac{1+y+y^2}{(1-y)^3} - 1 + 4\left(\frac{B}{b} - 1\right) y$$

$$= \frac{y(y^2 - 2y+4)}{(1-y)^3} + \left(\frac{B}{b} - 1\right) 4y$$

Since $y = \frac{b}{4V}$, $\frac{dV}{V} = - \frac{dy}{y}$. Thus

$$\int_{\infty}^{V} (Z-1)\, \frac{dV}{V} = - \int_{o}^{b/4V} \frac{y^2 - 2y+4}{(1-y)^3}\, dy - 4 \int_{o}^{b/4V} \left(\frac{B}{b} - 1\right) dy = I_1 + I_2$$

In I_1, let $1-y = x$ so that $dy = -dx$ and

$$I_1 = \int_{1}^{1-y} \frac{(1-X)^2 - 2(1-X)+4}{X^3}\, dX$$

$$= \int_{1}^{1-y} \frac{3}{X^3}\, dX + \int_{1}^{1-y} \frac{dX}{X} = - \frac{3}{2} \left[\left(\frac{1}{1-y}\right)^2 - 1\right] + \ln\,(1-y)$$

Since, obviously,

$$I_2 = -\ 4y(\frac{B}{b} - 1)$$

then

$$\int_{\infty}^{V} (Z-1)\ \frac{dV}{V} = -\ \frac{3}{2}\ [(\frac{1}{1-y})^2 - 1] + \ln\ (1-y) - 4y\ (\frac{B}{b} - 1) \qquad (18)$$

so that

$$\frac{A(V) - A^{(o)}(V)}{RT} = \frac{3n}{2}\ [(\frac{1}{1-y})^2 - 1] - n\ \ln\ (1-y) + 4ny(\frac{B}{b} - 1)$$

The non-ideal contribution to the chemical potential is then given by

$$\frac{\Delta\mu_i}{RT} = -\int_{\infty}^{V} (Z-1)\ \frac{dV}{V} - n\ \frac{\partial}{\partial n_i} \int_{\infty}^{V} (Z-1)\frac{dV}{V}$$

The first term has already been evaluated. The second is obtained by differentiating (18). Thus

$$\frac{\partial}{\partial n_i} \int_{\infty}^{V} (Z-1)\ \frac{dV}{V} = \left\{ -\ \frac{3}{2}\ \frac{(-2)(-1)}{(1-y)^3} - \frac{1}{1-y} - 4(\frac{B}{b} - 1) \right\} \frac{\partial y}{\partial n_i} - 4y\ \frac{\partial}{\partial n_i}(\frac{B}{b})$$

At this point use must be made of the one fluid model. Thus

$$\frac{\partial y}{\partial n_i} = \frac{1}{4V}\ \frac{\partial b}{\partial n_i} = \frac{1}{4V} \left[\frac{2 \sum\limits_j n_j\ b_{ij}}{(\Sigma\ n_i)^2} - \frac{2\ \Sigma\ n_i\ n_j\ b_{ij}}{(\Sigma\ n_i)^3} \right]$$

$$= \frac{1}{4V}\ \frac{2}{n} \left[\frac{\sum\limits_j n_j\ b_{ij}}{n} - b \right]$$

Also

$$\frac{\partial}{\partial n}(B/b) = \frac{1}{b}\frac{\partial B}{\partial n_i} - \frac{B}{b^2}\frac{\partial b}{\partial n_i}$$

Since, obviously, $\frac{\partial B}{\partial n_i}$ will have the same form as $\frac{\partial b}{\partial n_i}$ but with B replacing b, we can immediately write down

$$\frac{\partial}{\partial n_i}\left(\frac{B}{b}\right) = \frac{2}{n^2 b}\left[\sum_j n_j B_{ij} - \frac{B}{b}\sum_j n_j b_{ij}\right]$$

Combining all results obtained to here yields

$$\begin{aligned}\frac{\Delta\mu_i}{RT} = {} & \frac{3}{2}\left[\left(\frac{1}{1-y}\right)^2 - 1\right] - \ln(1-y) + 4\left(\frac{B}{b} - 1\right)y \\ & + \left[\frac{3}{(1-y)^3} + \frac{1}{1-y} + 4\left(\frac{B}{b} - 1\right)\right]\frac{2y}{b}\left[\frac{\sum_j n_j b_{ij}}{n} - b\right] \\ & + 4y\,\frac{2}{b}\left[\frac{\sum_j n_j B_{ij}}{n} - \frac{B}{b}\,\frac{\sum_j n_j b_{ij}}{n}\right]\end{aligned}$$

For simplicity we write this as

$$\frac{\Delta\mu_i}{RT} = \mu_o + \mu_1\,\frac{\sum_j n_j b_{ij}}{nb} + \mu_2\,\frac{\sum_j n_j B_{ij}}{nb}$$

where

$$\mu_o = \frac{3}{2}\left[\frac{1}{(1-y)^2} - 1\right] - \ln (1-y) - y\left[\frac{3}{(1-y)^3} + \frac{1}{1-y}\right]$$

$$\mu_1 = 2y\left[\frac{3}{(1-y)^3} + \frac{1}{1-y} - 4\right]$$

$$\mu_2 = 8y$$

Substitution in (17) then yields

$$\gamma_i' = \exp\left[- \omega_i \mu_o + \frac{\mu_1}{nb} \sum_\ell n_\ell \left(\sum_j v_{ij} b_{j\ell} - b_{i\ell}\right) + \frac{\mu_2}{nb} \sum_\ell n_\ell \left(\sum_j v_{ij} (B_{j\ell} - B_{i\ell})\right) /RT\right] \tag{19}$$

where $-\omega_i = \sum_j v_{ij} - 1$ is the net decrease in the number of particles in the i^{th} reaction defined earlier. With this expression for γ_i' it becomes possible to calculate the effect of the HS theory on the equilibrium composition of the mixture.

B. ENTROPY, ENTHALPY AND GIBBS FREE ENERGY

It is now possible to calculate all of the thermodynamic properties predicted for the HS model. The entropy follows from

$$S = -\left(\frac{\partial A}{\partial T}\right)_\rho$$

so that the real gas part is given by

$$\frac{\Delta S}{R} = -\left(\frac{\partial \Delta A}{\partial T}\right)_\rho = -\frac{\Delta A}{RT} - T\frac{\partial}{\partial T}\left(\frac{\Delta A}{RT}\right)_\rho$$

But

$$\frac{\partial}{\partial T}\left(\frac{\Delta A}{RT}\right)_\rho = n\left\{\frac{3}{(1-y)^3} + \frac{1}{1-y} + 4\left(\frac{B}{b} - 1\right)\right\}\left(\frac{\partial y}{\partial T}\right)_\rho$$

$$+ 4ny\frac{\partial}{\partial T}\left(\frac{B}{b}\right)_\rho$$

Now $\left(\frac{\partial y}{\partial T}\right)_\rho = \frac{\rho}{4}\frac{\partial b}{\partial T}$

and $\frac{\partial}{\partial T}\left(\frac{B}{b}\right) = \frac{1}{b}\frac{\partial B}{\partial T} - \frac{B}{b^2}\frac{\partial b}{\partial T}$

so that $\frac{\partial}{\partial T}\left(\frac{\Delta A}{RT}\right) = \left\{\frac{3}{(1-y)^3} + \frac{1}{1-y} - 4\right\}\frac{y}{b}\frac{\partial b}{\partial T} + \frac{4y}{b}\frac{\partial B}{\partial T}$

Thus

$$\frac{\Delta S}{R} = \frac{3n}{2}\left[\left(\frac{1}{1-y}\right)^2 - 1\right] - n\,\ln(1-y) + 4\,n\,y\left(\frac{B}{b} - 1\right)$$

$$+ \left\{\frac{3}{(1-y)^3} + \frac{1}{1-y} - 4\right\}\frac{nyT}{b}\frac{\partial b}{\partial T} + \frac{4yT}{b}\frac{\partial B}{\partial T}$$

$\frac{\partial b}{\partial T}$ and $\frac{\partial B}{\partial T}$ are expected to be quite small because of the high temperatures of interest. It is therefore possible that the last two terms might be negligible with respect to the first three. This would need to be examined, however.

This expression for the entropy and the earlier one for the equation of state can be used to calculate the enthalpy and Gibbs free energy. Specific heats can be calculated from these functions either by numerical differentiation or by means of algebraic expressions which can be derived by differentiation of the above expressions[3].

V. NUMERICAL METHODS

The primary step in calculating the thermodynamic properties consists of the determination of the equilibrium composition of the mixture. This requires the solution of equations (1) subject to the constraint that the total mass of each nuclear type be conserved. The effective activity coefficients, γ_i', are given by equation (19) for the contribution of the HS model to the equilibrium constant and in appendix B of reference (3) for that of the Debye-Hückel theory of ionic solutions. There are two lower level approximations to the HS model which we have already considered in earlier work. We have already used the ideal gas approximation, in which all γ_i' are taken equal to unity. We have also made use of the second virial coefficient approximation for which the γ_i' of the HS model are replaced by the term linear in the density in their density expansions (which term appears in appendix B of reference (3)).

The method used for the solution of the equations for the concentrations in both the ideal gas and second virial gas has been described in some detail elsewhere.[3] The procedure used here was required to be applicable to all three approximations, i.e. the ideal gas, second virial and HS. Although based on these earlier methods,there was a considerable modification of certain details of the original approach to allow for greater flexibility in obtaining solutions. In order to permit reference species to be chosen at will simply through modification of the input data (as described in reference (3)), the calculation of the equilibrium constants was made part of the computer program. This led to the discovery of an error in the equilibrium constant used for O_2^- in the previous NBS tables. Our correction of this error caused the search method used for finding the electron concentration to be unstable at low temperatures. A not insignificant amount of time was spend in isolating this problem and in correcting it. The problem was associated with orders of magnitude increase in the concentration of O_2^- which occurred after the correction was inserted. As a result, the electron concentration now became orders of magnitude smaller than the concentration of O_2^- and, in fact, was now calculated as a small difference between the concentrations of NO^+ and O_2^-. This often led to negative interim values for the electron concentration during the non-linear search procedure. Since the electron concentration has only a minor effect on the values obtained for the other reference species, the problem was solved by instituting a grid search for the electron concentrations, over positive values only, whenever a negative guess value was obtained for that concentration, leaving all other concentrations fixed at their current values.

At low temperatures, it was also necessary to produce a very strong "damping" of the electron concentration by means of a q value[3] smaller than (but in the neighborhood of) unity. This reduced the "natural" excursions in the electron concentration from iteration to iteration.

Initially, precisely the same search procedure was used for the HS model as was used earlier for the ideal and second virial gases except that the γ_i' for the HS model now had to be computed at each iteration. Problems arose, however, because these γ_i' became quite large for certain species at the highest densities. In fact, γ_i' values approaching 10^6 were encountered. This produced instabilities in the search procedure used. This problem was solved by what might be called a dual level search procedure. In this procedure an initial set of γ_i' were computed based on the initial guesses. These γ_i' were maintained constant until a set of concentrations was obtained which satisfied the mass balance equations for the gas with these initial γ_i' values. With these concentrations, a new set of γ_i' was computed. These new γ_i' were now held constant and a second set of concentrations obtained which satisfied the mass balance equations for this second set of γ_i' values. The procedure was carried out repeatedly until the largest change in the γ_i' when recomputed was less than a given tolerance. To reduce the possibility of producing numerical instabilities, only a fraction of the change calculated for each γ_i' was used in any new iteration and, in any case, the γ_i' were not allowed to change by more than some arbitrary factor. In order to reduce the computer time required, a coarse tolerance was placed on the values of the concentrations accepted as correct for the first few sets of values (generally incorrect) obtained for the γ_i' in this procedure.

The present computer program has, to a large extent, retained the ability of the earlier program to obtain solutions essentially independent of the initial guess values for the concentrations of the reference species. The electron concentration is perhaps an exception to this but then mainly only when the computation on an isotherm begins at quite high densities.

Since the few problems which we have encountered with obtaining solutions must depend on the specific search procedure used by us, it would be useful to study the process of solution for other search procedures. Because of its simplicity, we would place particular emphasis on a study of the direct search method of Hooke and Jeeves[31].

Once the species concentrations are obtained in the above manner (with the mass balance equations satisfied to the tolerances specified for each reference species), the thermodynamic properties of the mixture can be calculated in a straightforward manner.

VI. RESULTS

In this section we discuss a number of special features of the results obtained, reserving our discussion to those results which illustrate the effects of density. We compare results obtained by us for the ideal gas, second virial coefficient and HS models with each other and, where appropriate, with the results of the GB extrapolation. We shall also compare the concentrations predicted for various species among the three approximations used by us. The Grabau-Brahinsky model[8] does not include the calculation of the species concentrations so cannot be included in that part of the discussion.

Certain interesting features of the predicted dependence of the concentrations on density are also discussed. Of particular interest is the demonstration of the "strength" of Le Chatelier's principle[32].

A. THE DEPENDENCE OF SPECIES CONCENTRATIONS ON DENSITY.

The formalism which we have developed has the capability of predicting density effects on species concentrations. This ability is important for two reasons. It is obviously important when the concentrations of the species themselves are needed, as might be the case when specific species have particularly interesting properties. Examples might be the electrically charged species (which obviously affect the electrical conductivity very strongly) and any species which radiate in a useful part of the spectrum. Being able to predict density effects on concentrations is also important in the calculation of the density effects on the thermodynamic properties. The expressions for the thermodynamic properties of the reacting mixture are sums over concentrations times properties of individual species plus sums of products of concentrations times properties of pairs of species. In our model, the latter enter into the calculation of the average (i.e. one fluid) molecular diameter. The thermodynamic properties of the mixture therefore depend on temperature and pressure through the dependence of the concentrations on these state parameters.

Density effects on the thermodynamic properties of air have generally been calculated by others on the assumption that the species concentrations either do not change with density or simply obey the ideal gas mass action law. This was essentially the assumption of Grabau and Brahinsky. As we shall show, this kind of assumption breaks down, particularly at the highest densities where the identities of the major species in the mixture change, when density effects are specifically taken into account. This can change the entire character of the gas being studied.

Care must be taken here not to place too much emphasis on the actual numerical values obtained by us for the concentrations. The species concentrations at high densities are expected to be sensitive functions of the assumptions made in any calculation of this kind. In our model, they can be expected to depend very strongly on the intermolecular forces used (especially at the highest densities) as well as on the method of calculating the hard sphere diameter at temperatures for which the second virial coefficient has a negative slope. This problem is associated with the fact that the effective hard core potential produces a second virial coefficient whose slope is always positive. The relationship of the actual numerical values obtained by us to actual air might also be expected to depend strongly on our omission of such species as N_2O_4, C_2, O_3 and some of the molecular ions.

Because of Le Chatelier's principle, errors introduced into the calculation of the concentrations for any one of these reasons should be less than that which might be estimated from a direct calculation of the apparent effect of the omission. This principle is essentially a statement of the competition among the various chemical reactions, because of which species concentrations "resist" change. Thus, suppose a correction to the equilibrium constant in a certain reaction produces an increase in the concentration of a particular species. This increase will cause a competing reaction containing that same species to move in such a direction as to reduce the concentration of this particular species. The overall effect of the original correction to the equilibrium constant is thereby reduced. An example of this is described below. Because of this and because any errors resulting from our various assumptions can be expected to affect the different species perhaps randomly according to sign, the overall effects of our zeroth order assumptions on the properties computed should actually be much smaller than might be expected from an examination of the effects of the various separate approximating assumptions. This error reduction might be considered to be a decided advantage in favor of the use of a microscopic molecular model such as ours.

The operation of Le Chatelier's principle can be seen by comparing the change in various concentrations actually obtained in the calculation when the density is changed at constant temperature with that which might have been expected from the change in the density factor $(\rho/\rho_o)^{-\omega_i}$ in equation (1). Consider, for example, going from log $\rho/\rho_o = 2.0$ to 3.0 at T = 3000K. For the species N_2O, a concentration enhancement by a factor of 1.6×10^5 could have been expected based on the value $\gamma_i' = 4.3 \times 10^4$ at log $\rho/\rho_o = 3.0$ and $\omega_i = 0.5$, whereas the actual enhancement obtained involved only a factor of 1.7×10^3. There was, therefore, a reduction by a factor of 100.

Figures 16 and 17 contain plots of concentrations against density for a number of species for the temperatures 3000K and 9000K. The concentrations are those which were calculated using the full density effect with the HS equation, and those based on the ideal gas.

The dependence on density of the concentration of oxygen and the effect of this dependence on the concentration of the other species are particularly interesting. The rapid decrease in the concentration of molecular oxygen at the highest densities is very dramatic for the HS gas, especially when compared to its behavior in the other two approximations. As a result, the gas at 3000K and 1000 times normal density consists mainly of N_2 and NO rather than of N_2 and O_2 as predicted in the ideal gas approximation. Secondary effects from this reduction in O_2 concentration can be seen in the marked reduction in the concentrations of O_2^-, O_2^+ and O^- predicted by the HS theory as compared to the predictions of the ideal gas approximation.

The reduction in O_2 concentration "results" from the enhancement in the production of NO, NO_2 and N_2O and the associated requirement for the production of atomic oxygen for the formation of these species. The cause of the enhancement of these species can be seen in Table 2 which contains the γ_i' values for all species at T = 3000K for several densities. In the concentration units used by us, it is necessary to multiply the γ_i' by $(\rho/\rho_o)^{-\omega_i}$ to obtain the full density effect along an isotherm. As is pointed out below, in some instances this produces enhancement factors of 10^6 for the equilibrium constant.

An interesting effect, which might be called a second order effect of the reduction in O_2 concentration, was seen among the carbon containing compounds. According to the γ_i' values of Table 2, the concentration of C should drop drastically with increasing density. This is especially true when the factor $(\rho/\rho_o)^{-1}$ is added (bringing in an additional factor of 10^{-3} at the highest density). Instead, the concentration of C increases slightly with density. This comes about because the reduction in O_2 concentration causes a decrease in the production of CO_2. This "frees" carbon atoms which become available for the enhancement of the CO and C concentrations.

Another second order effect is that of the slight increase in electron concentration with increasing density, quite the opposite of the ideal gas behavior. This results from the decrease in the concentrations of O_2^- and O^- which results in additional free electrons. The increase in the electron concentration, in turn, results in a drop in the concentration of NO^+, the main electron producer, causing the increase in electron concentration to be somewhat reduced from that expected purely on the basis of reduction in O_2^-, another example of Le Chatelier's principle.

Those species for which γ_i' has the value of unity in Table 1 are either reference species, for which no equilibrium constant is needed, or are ions for which no estimates of virial coefficients were available. It should be noted that the γ_i' values for the species N_2O and NO_2 begin to approach 10^5 at the highest densities. This effect is further enhanced by the factor 33 for each arising from the factor $(\rho/\rho_o)^{-1/2}$. The overall density effect for these species at $\rho/\rho_o = 1000$ as compared to $\rho/\rho_o = 1.0$ is then such as to multipy the equilibrium constant by a factor of over 10^6. It is therefore obvious why there is such a strong dependence of concentration on density.

The competition at the highest densities among NO, NO_2 and N_2O (and especially between the last two) is particularly interesting. As the density increases, all three species' concentrations increase. At 3000K this occurs mainly at the expense of molecular oxygen. As the density increases, however, the enhancement of N_2O begins to proceed at such a pace as to "require" oxygen atoms from other reactions so that, ultimately, the increase in N_2O concentration takes place at the expense of the concentrations of NO_2, CO_2 and NO. At 9000K, the initial enhancement occurs at the expense of the oxygen atom concentration but, at intermediate densities, produces a reduction in molecular oxygen concentration. Eventually, the increased N_2O concentration occurs as a result of a reduction in NO and NO_2 concentrations.

The absence of estimates of the virials for interactions involving ionic species obviously leads to errors at the highest temperatures where charged species become non-negligible. Although these charged species do not dominate in our approximation, it is conceivable that they might become major constituents through enhancements caused by large γ_i' values which might be obtained. This effect might be expected to be smaller for the ionic species than it was for the neutrals NO, NO_2 etc. for two reasons. First of all, even at high temperatures, repulsion between ions of like sign is reduced by the effects of attraction between those of opposite sign. Secondly, our inclusion of the Debye-Hückel limiting law (see reference (3)) already includes part of the interaction between charged particles.

B. DENSITY EFFECTS ON THE EQUATION OF STATE.

Table 3 contains the compressibility factor as a function of density at selected temperatures for all three approximations as well as for that of Grabau and Brahinsky. The ideal gas approximation contains no correction to the equation of state for the effect of density. Since there is a "density effect" in the law of mass action as written in the units used by us there is a variation in the calculated compressibility factor with density. By our definition, the compressibility factor for the ideal gas is simply the total number of moles of the mixture. According to the equations of chemical equilibrium for the ideal gas as written in our units, the effective equilibrium constant for a particular reaction in the ideal gas approximation is given by $K_i^{eff} = K_i\,(T/T_0)^{\omega_i}\,(\rho/\rho_o)^{-\omega_i}$ and so increases with density for those reactions in which a net decrease in the number of particles results in the production, from the reference species, of the species associated with the reaction. Such a reaction, for example, is

$$N_2O = N_2 + \frac{1}{2} O_2$$

where two molecules are produced for every three which react. On the other hand, a reaction for which there is a net increase in particles has an equilibrium constant which decreases with density. An example is

$$O = \frac{1}{2} O_2$$

where two oxygen atoms are produced for each molecule of molecular oxygen. The net result of this combination of enhanced effective equilibrium constant with density for reactions in which the number of particles is decreased and decreased effective equilibrium constant with density for those in which it is increased is to produce a decrease in the total number of particles with density - a result which is clearly visible in Table 3.

With very few exceptions (e.g. some of the ionic species) all virial coefficients are expected to be positive at the temperatures of interest (and, in fact, even at much lower temperatures). It is for this reason that the HS model is expected to be particularly appropriate here. Because of this positive behavior, at these temperatures density corrections to the equation of state must be positive at all densities and are required to increase with density. Any approximation which has this character must therefore produce a density correction to the ideal gas which has the correct sign, if not the proper magnitude. The simplest such correction is associated with taking only the second virial coefficient. According to Table 3, such an approximation does produce an increase in compressibility factor with density for the intermolecular potential functions used here since these produce positive second virial coefficients. The decrease in the magnitude of this correction with increasing temperature at constant density is caused by a reduction with increasing temperature in the magnitude of the second virial coefficient for many of the interactions used since the temperatures of interest are above those at which the second virial coefficients for these interactions exhibit maxima.

The GB approximation is strongly dependent on our second virial coefficients, since those authors made use of our earlier results for the second virial gas to tie down their extrapolations at 5000 and 6000 kelvins. For this reason, their predictions should be in close agreement with the results for the second virial gas up to the densities at which that approximation is expected to be valid or to densities somewhat below 100 amagats. This is essentially the behavior exhibited in Table 3. Since the GB model is based on the results of our second virial approximation, this agreement is not a test of the GB model but rather serves as a test of the computer program developed by those authors as well as of our own and as a test of the GB input data as obtained from our virials. Since their approximation includes an estimate for the effect of third virial coefficients and since the HS approximation does also, and since both of these are of the same sign, the predictions of the GB calculation should be expected to agree with results for the HS model to slightly higher densities than the second virial gas (and this is also exhibited in Table 3).

Our present results are entirely compatible with the predictions of the second virial gas. This is no more than expected since both calculations were based on the same second virial coefficients and since our model reduces exactly to the second virial gas in the limit of low density when all but linear density terms are neglected.

As the density increases beyond approximately 100 amagats, our results for the HS model begin to deviate very rapidly from the second virial results, becoming over twice as large at a density of 1000 times normal. It should be noted that there is a similar relationship between the results for the GB approximation and those for the second virial gas except that since those two approaches involve very similar approximations, differences between their results are considerably smaller than between the HS and second virial approaches, especially at the highest densities.

C. SUGGESTED POSSIBILITIES FOR IMPROVEMENTS IN THE TABLES.

As mentioned above, a number of approximations were made in order to expedite the completion of these calculations. These approximations were considered to be sufficiently minor so as not to affect a study of the effect of density corrections on the concentrations and of the feasibility of carrying out such calculations. Because of the nature of the calculation and because of the applicability of Le Chatelier's principle, most of the approximations should not be expected to affect the accuracy of the compressibility factors drastically. In this section we shall describe ways in which these approximations might be relaxed in order to produce more accurate tables. Please note that the order in which the approximations are discussed is not necessarily related to the order of their importance.

In this calculation we include only the compressibility factor from among the thermodynamic properties. Thermodynamic properties can be obtained either through numerical operations on our tables of compressibility factors or through direct calculation of the properties from the equations given in the text. For some of the properties, such direct calculations require a knowledge of the temperature derivatives of the temperature dependent parameters associated with the effective potential function, i.e. $b(T)$ and $\varepsilon(T)$, particularly the first. This, in turn, requires an improvement in the method used for the calculation of the hard sphere diameters for temperatures above that at which the second virial coefficient attains its maximum. While the method used by us produces a relatively trivial discontinuity in the value of b(T) at the change-over temperature, it does produce a discontinuity in its temperature derivative which is much larger. It is clearly possible that these discontinuities in the values of $\frac{db_{ij}}{dT}$ will also be reflected in dZ/dT values obtained in a numerical differentiation. Hence, even though it might be possible to neglect the temperature derivative of b(T) as being small, it is probably very necessary to improve on the method of calculating b(T) at high temperatures to ensure that spurious discontinuities in slope are not introduced.

There are a number of methods which could be used for the calculation of b(T) for temperatures above that at which the second virial attains a maximum and these should be investigated. Since the effect of attraction can be totally neglected at these temperatures, the most promising method might be one in which the problem of finding the two parameters b(T) and ε(T) at each temperature is replaced by that of obtaining b(T) only. The present method essentially does this but in a very arbitrary manner, and must be modified so as to produce a smooth table of values for db/dT.

An obvious improvement in the tables will also result when the intermolecular potentials used by us are replaced by improved ones. The most important of these have already been determined by us in earlier work under this contract. In an earlier report, we estimated the possible effect of this on calculated tables. Although the effect was shown to be considerably smaller than were the substantial differences reported here between our results and those of the GB model, they were nevertheless found to be not negligible. Such a study needs to be made within the context of the HS theory, it being otherwise impossible to place meaningful estimates of precision on our results. For the second virial coefficient alone, the ratio of the value predicted for the (18,6) potential to that predicted for the (12,6) at a temperature of 5000° when the value at 500° is correctly predicted by both, is given approximately by

$$\left(\frac{5000}{500}\right)^{\frac{2}{18}-\frac{2}{12}} = (10)^{-\frac{1}{18}}$$

for a difference of approximately 14%.

Those properties which depend on db/dT would probably only be modified slightly by changing the potentials since db/dT is small for almost all potentials at the temperatures of interest. In our earlier report[27] this was shown to be true for the first density corrections to such properties.

Improvement of the tables through the improvement of certain of the intermolecular potentials used (e.g. pair interactions involving NO_2) would take considerable additional effort. This would require a literature search for experimental data for second virial coefficients and viscosity data for the relevant species and the determination of parameters for intermolecular forces using such data.

Related to this but somewhat broader in scope is the need for a detailed study of mixing rules by means of which potential functions which describe the interactions between unlike species are inferred from those which describe the interactions between like species. This is particularly important for such pairs as N_2- NO which are major constituents under the conditions of interest.

One of the unexpected problems which we met in this work had to do with the need for having enough interaction virials for the description of the interactions between a given major species and other important species. Because the net effect of these interactions on the equilibrium constant generally appears as a smaller difference between larger quantities, such quantities cannot be arbitrarily neglected. We solved this problem partly by a shift to other reference species and partly by arbitrary approximation of the unknown interactions. A study needs to be made to establish a criterion for determining when such interactions can be neglected. The importance of this can be seen from the sheer number of possible interactions which can be needed in a calculation of this kind. Thus, in a mixture of n constituents there are $n(n+1)/2$ pair interactions. A mixture of 30 species therefore has 465 possible pair interactions!! The determination of these would constitute a tremendous job made particularly difficult in our case by the facts that data are not available for the appropriate binary mixtures (since many of these species cannot be handled at ordinary temperatures while other species are not available in more than trivial concentrations at equilibrium at such temperatures). This is, for example, true of the atomic species. Another major problem comes from the fact that of the 465 pairs, 435 involve interactions between unlike species. The possibility of there being data on the 435 binary mixtures needed at a sufficient number of temperatures and for a sufficient number of relative concentrations from which to infer potentials of interaction is extremely small. Thus, many of the interactions need to be estimated by whatever means is available. Clearly, any reduction in the number of pair interactions needed and in the accuracy with which the remaining ones are needed produces a comparable direct reduction in the amount of work involved in calculations of this kind. Thus, criteria need to be established, within the framework of our model, by means of which it can be determined when a particular pair interaction can be neglected and when a pair interaction contributes sufficiently little so that it can be approximated in a rather cavalier fashion.

Table 1. Q* Values for the (12,6) Hard Core Potential

T*	Q*	T*	Q*	T*	Q*
0.90	-0.60070	3.5	-0.02795	8.4	1.38388
0.95	-0.59951	3.6	-0.00024	8.8	1.50111
1.00	-0.59705	3.7	0.02759	9.0	1.55976
1.20	-0.57737	3.8	0.05550	9.2	1.61844
1.30	-0.56310	3.9	0.08351	9.4	1.67715
1.40	-0.54667	4.0	0.11159	9.6	1.73588
1.50	-0.52851	4.4	0.22464	9.8	1.79463
1.60	-0.50893	4.6	0.28153	10.0	1.85341
1.70	-0.58818	4.8	0.33861	11.0	2.14753
1.80	-0.46656	5.0	0.39587	11.5	2.29474
1.90	-0.44389	5.2	0.45328	12.0	2.44202
2.00	-0.42062	5.4	0.51083	12.5	2.58939
2.10	-0.39675	5.6	0.56850	13.0	2.73679
2.20	-0.37236	5.8	0.62629	13.5	2.88426
2.30	-0.34751	6.0	0.68417	14.0	3.03178
2.40	-0.32226	6.2	0.74214	14.5	3.17934
2.50	-0.29666	6.4	0.80019	15.0	3.32694
2.60	-0.27075	6.6	0.85832	15.5	3.47458
2.70	-0.24456	6.8	0.91651	16.0	3.62225
2.80	-0.21812	7.0	0.97476	16.5	3.76994
2.90	-0.19147	7.2	1.03307	17.0	3.91767
3.00	-0.16461	7.4	1.09143	17.5	4.06542
3.10	-0.13758	7.6	1.14984	18.0	4.21319
3.20	-0.11038	7.8	1.20829	18.5	4.36098
3.30	-0.08304	8.0	1.20829	19.0	4.50879
3.40	-0.05556	8.2	1.32532	19.5	4.65661
				20.0	4.80446

Table 2: γ_3' Values for Several Densities for Representative Species

Species	log ρ/ρ_0 0.0	1.0	2.0	2.4	2.8	2.9	2.95	3.0
C	0.9978	0.9784	0.7869	0.4965	0.0598	0.0083	0.0015	0.0001
O	0.9992	0.9923	0.9268	0.8353	0.6900	0.6297	0.5904	0.5278
N	0.9991	0.9912	0.9163	0.8111	0.6365	0.5715	0.5338	0.4824
O^-	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
NO^+	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
N_2O	1.0001	1.0016	1.0575	1.4128	19.4924	383.1603	5879.5	43450.
NO_2	1.0000	1.0005	1.0445	1.3580	16.2103	278.0573	3786.1	221998.
CO_2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
CO	0.9989	0.9886	0.8959	0.7808	0.6912	0.7177	0.7651	0.8457
NO	0.9999	0.9997	1.0225	1.2001	5.6625	32.0525	156.53	1803.98

Table 3. Comparisons of the Compressibility Factors, PV/RT for Air for Four Approximations (Including that of Grabau and Brahinsky) as Functions of Density at Various Temperatures

		T = 3000 K				T = 6000 K			
log ρ/ρ_o	ρ/ρ_o	Ideal	2nd Vir.	H.S.	GB	Ideal	2nd Vir.	H.S.	GB
0.0	1.000	1.00716	1.00860	1.00860	1.00860	1.19771	1.19933	1.19932	1.19931
1.00	10.000	1.00216	1.01657	1.01670	1.01671	1.12652	1.14152	1.14167	1.14165
2.00	100.000	1.00026	1.14431	1.15822	1.15971	1.05716	1.19883	1.21259	1.21076
2.20	158.489	0.99999	1.22827	1.26474	1.26702	1.04694	1.26982	1.30521	1.29973
2.40	251.189	0.99971	1.36150	1.45984	1.45689	1.03811	1.38913	1.48281	1.41913
2.60	398.107	0.99943	1.57279	1.85170	1.83684	1.03055	1.58387	1.84433	1.73683
2.80	630.957	0.99911	1.90779	2.78587	2.61764	1.02411	1.89703	2.68901	2.36473
3.00	1000.000	0.99875	2.43885	5.86038	4.39136	1.01863	2.39685	5.29604	3.59066

Table 4. Compressibility Factors, PV/RT, for Air for Three Approximations as Functions of Density at Various Temperatures

		T = 2000 K			T - 3000 K			T = 4000 K		
log ρ/ρ_o	ρ/ρ_o	Ideal	2nd Vir.	H.S.	Ideal	2nd Vir.	H.S.	Ideal	2nd Vir.	H.S.
0.0	1.000	1.00003	1.00147	1.00147	1.00716	1.00860	1.00860	1.06259	1.06406	1.06406
0.50	3.162	0.99999	1.00453	1.00454	1.00400	1.00856	1.00858	1.03838	1.04297	1.04299
1.00	10.000	0.99995	1.01429	1.01443	1.00216	1.01657	1.01670	1.02258	1.03697	1.03710
1.50	31.623	0.99989	1.04522	1.04668	1.00103	1.04660	1.04793	1.01282	1.05808	1.05940
2.00	100.000	0.99980	1.14313	1.15847	1.00026	1.14431	1.15822	1.00689	1.14954	1.16327
2.20	158.489	0.99974	1.22692	1.26722	0.99999	1.22827	1.26474	1.00519	1.23109	1.26696
2.40	251.189	0.99968	1.35972	1.46876	0.99971	1.36150	1.45984	1.00376	1.36152	1.45801
2.60	398.107	0.99959	1.57022	1.88108	0.99943	1.57279	1.85170	1.00252	1.56918	1.84263
2.80	630.957	0.99948	1.90387	2.88947	0.99911	1.90779	2.78587	1.00141	1.89904	2.76067
2.85	707.946	0.99945	2.01418	3.38046	0.99902	2.01857	3.22655	1.00114	2.00819	3.18815
2.90	794.328	0.99941	2.13797	4.10655	0.99894	2.14287	3.83243	1.00088	2.13068	3.76453
2.95	891.251	0.99938	2.27685	5.16701	0.99884	2.28235	4.67103	1.00063	2.26815	3.76453
3.00	1000.000	0.99934	2.43269	6.74005	0.99875	2.43885	5.86038	1.00037	2.42241	5.67075

		T = 5000 K			T = 6000 K			T = 7000 K		
0.0	1.000	1.14410	1.14566	1.14566	1.19771	1.19933	1.19932	1.26975	1.27145	1.27142
0.50	3.162	1.10701	1.11176	1.11178	1.16425	1.16918	1.16919	1.21977	1.22481	1.22482
1.00	10.000	1.07208	1.08669	1.08683	1.12652	1.14152	1.14167	1.17562	1.19096	1.19111
1.50	31.623	1.04503	1.09036	1.09171	1.08877	1.13467	1.13605	1.13236	1.17900	1.18043
2.00	100.000	1.02654	1.16822	1.18190	1.05716	1.19883	1.21259	1.09191	1.23433	1.24822
2.20	158.489	1.02112	1.24492	1.28043	1.04694	1.26982	1.30521	1.07758	1.30063	1.33603
2.40	251.189	1.01660	1.37031	1.46520	1.03811	1.38913	1.48281	1.06464	1.41441	1.50716
2.60	398.107	1.01280	1.57208	1.83911	1.03055	1.58387	1.84433	1.05317	1.60231	1.85660
2.80	630.957	1.00959	1.89425	2.72389	1.02411	1.89703	2.68901	1.04315	1.90629	2.66258
2.85	707.946	1.00887	2.00103	3.12882	1.02266	2.00108	3.07032	1.04086	2.00750	3.02267
2.90	794.328	1.00817	2.12093	3.67196	1.02127	2.11800	3.58090	1.03865	2.12127	3.50419
2.95	891.251	1.00749	2.25554	4.42148	1.01992	2.24934	4.28637	1.03653	2.24934	4.28637
3.00	1000.000	1.00684	2.40665	5.48858	1.01863	2.39685	5.29604	1.03448	2.39279	5.12396

Table 4. Compressibility Factors, PV/RT, for Air for Three Approximations as Functions of Density at Various Temperatures (Continued)

		T = 8000 K			T = 9000 K			T = 10000 K		
$\log \rho/\rho_o$	ρ/ρ_o	Ideal	2nd Vir.	H.S.	Ideal	2nd Vir.	H.S.	Ideal	2nd Vir.	H.S.
0.0	1.000	1.39887	1.40073	1.40067	1.57870	1.58092	1.58081	1.75557	1.75831	1.75824
0.50	3.162	1.30590	1.31111	1.31113	1.43559	1.44113	1.44115	1.59299	1.59914	1.59917
1.00	10.000	1.23653	1.25221	1.25238	1.32462	1.34084	1.34103	1.44170	1.45884	1.45907
1.50	31.623	1.17952	1.22691	1.22840	1.24034	1.28868	1.29031	1.32093	1.37070	1.37253
2.00	100.000	1.12922	1.27275	1.28692	1.17308	1.31801	1.33279	1.22803	1.37491	1.39075
2.20	158.489	1.11104	1.33491	1.37064	1.14966	1.37478	1.41150	1.19695	1.42384	1.46246
2.40	251.189	1.09423	1.44376	1.53628	1.12811	1.47801	1.57167	1.16880	1.51948	1.61621
2.60	398.107	1.07895	1.62527	1.87516	1.10846	1.65256	1.90147	1.14341	1.68489	1.93760
2.80	630.957	1.06530	1.92006	2.64817	1.09075	1.93623	2.64864	1.12063		2.66597
2.85	707.946	1.06214	2.01822	2.99064	1.08663	2.02946	2.97754	1.11534		2.98550
2.90	794.328	1.05909	2.12851	3.44787	1.08263		3.41590	1.11021		3.41076
2.95	891.251	1.05613	2.25225	4.07983	1.07875		4.02162	1.10522		3.99831
3.00	1000.000	1.05327	2.39069	4.98634	1.07500		4.89104	1.10040		4.84254

		T = 11000 K			T = 12000 K			T = 13000 K		
0.0	1.000	1.88065	1.88393	1.88443	1.95523	1.95864	1.95864	2.00423	2.00857	2.00857
0.50	3.162	1.74179	1.74884	1.74889	1.85446	1.86238	1.86242	1.92978	1.93876	1.93880
1.00	10.000	1.57443	1.59300	1.59327	1.70139	1.72172	1.72205	1.80573	1.82806	1.82842
1.50	31.623	1.41996	1.47187	1.47400	1.52904	1.58386	1.58635	1.63623	1.69460	1.69746
2.00	100.000	1.29616	1.44580	1.46322	1.37588	1.52919	1.54866	1.46252	1.62015	1.64206
2.20	158.489	1.25511	1.48445	1.52602	1.32372	1.55620	1.60160	1.39995	1.63541	1.68573
2.40	251.189	1.21833	1.56995	1.67196	1.27688	1.62873	1.73815	1.34289	1.69073	1.80986
2.60	398.107	1.18548	1.72117	1.98433	1.23514	1.73950	2.03625			
2.80	630.957	1.15627		2.70028	1.19818		2.74512			
2.85	707.946	1.14951		3.01484	1.18964		3.06156			
2.90	794.328	1.14295		3.43301	1.18138		3.47979			
2.95	891.251	1.13660		4.01070	1.17339		4.05639			
3.00	1000.000	1.13045		4.84201	1.16566		4.88690			

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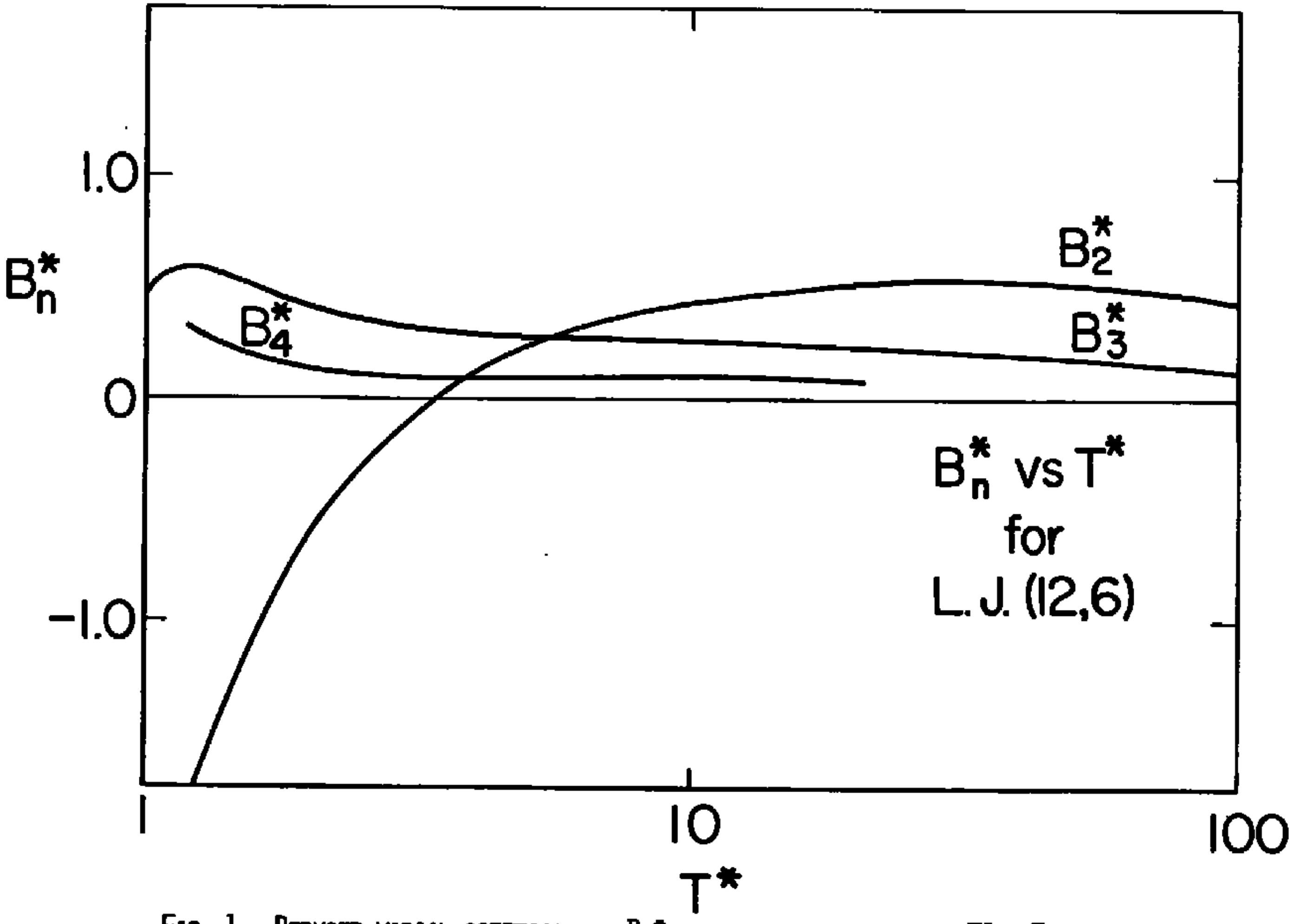

Fig. 1. Reduced virial coefficients B_N^* vs reduced temperature T^*. The maxima tend to lower temperatures with increasing N, supporting the argument made in the text that, except at low temperatures, the higher virials are representable by hard-sphere interactions without attraction.

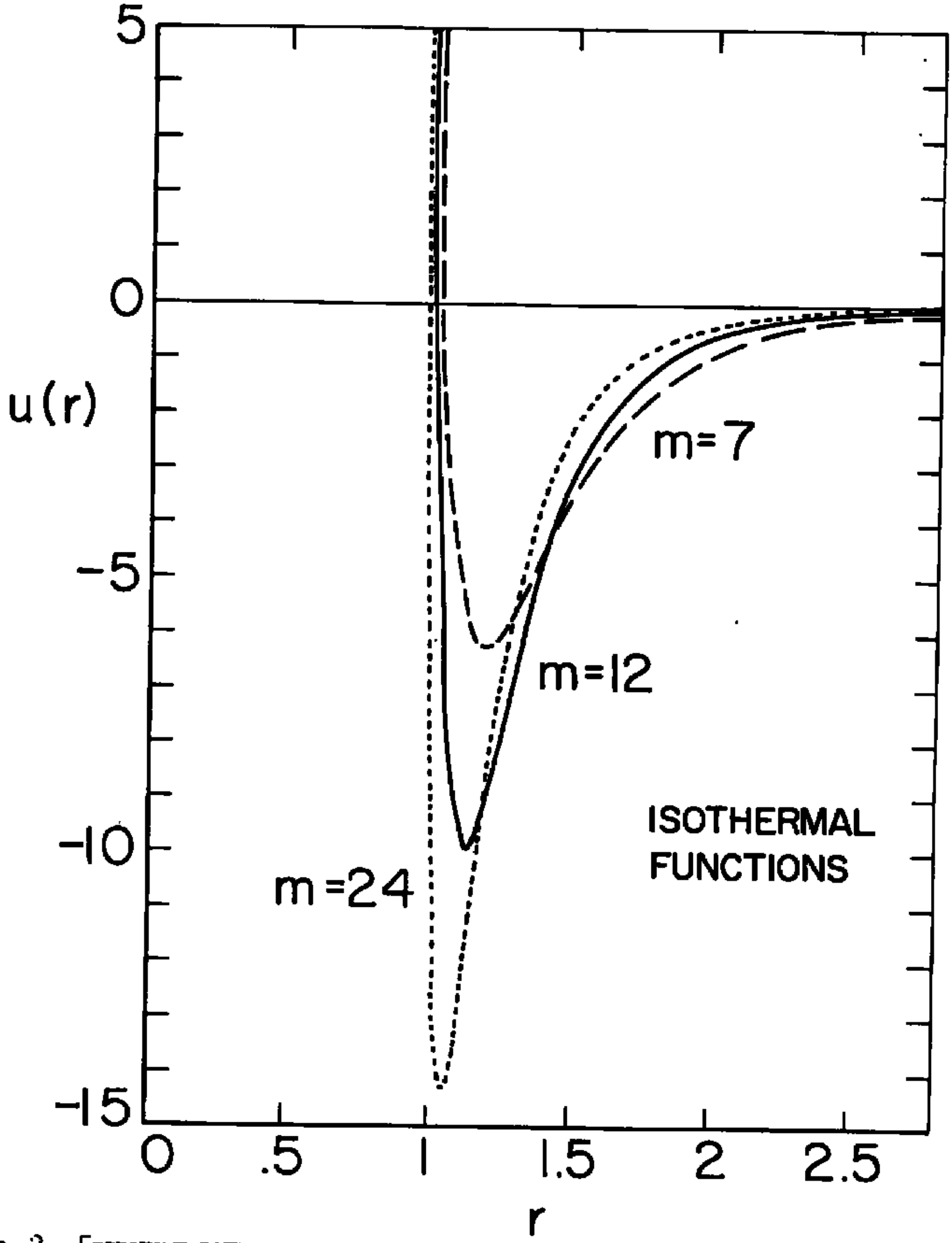

FIG. 2. EFFECTIVE POTENTIALS VS MOLECULAR SEPARATION IN ARBITRARY UNITS FOR SEVERAL VALUES OF M AND FOR $T^* = 2.5$. IT IS SEEN THAT THOUGH THE SHAPE OF THE "BOWL" IS QUITE SENSITIVE TO THE CHARACTERISTIC PARAMETER M, THE SPHERE DIAMETER AT THIS TEMPERATURE IS ONLY WEAKLY SENSITIVE TO IT.

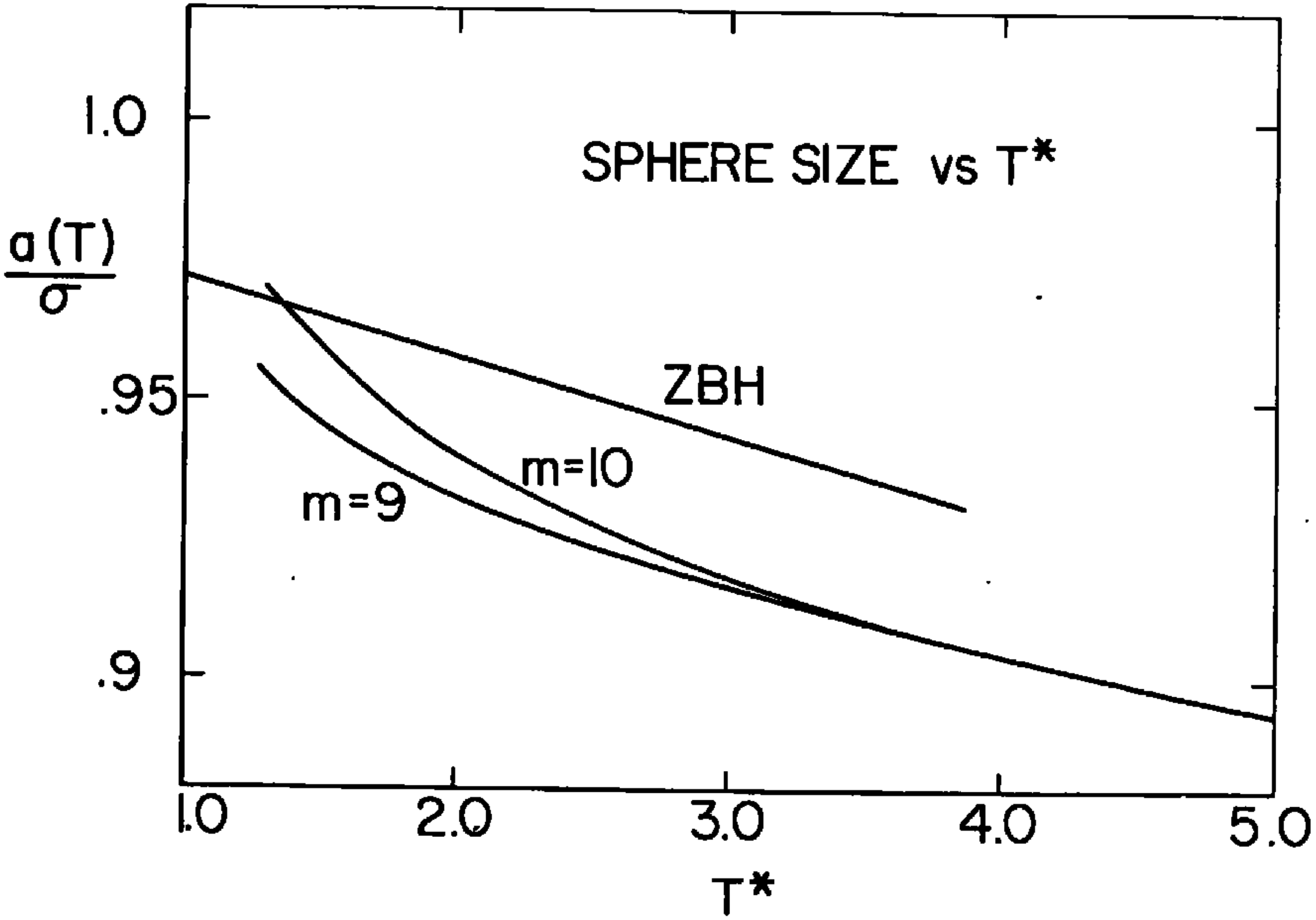

FIG. 3. THE SPHERE DIAMETER IN REDUCED UNITS VS REDUCED TEMPERATURE FOR EFFECTIVE POTENTIALS WITH M=9 AND M=10 AND FOR THE ZBH THEORY.

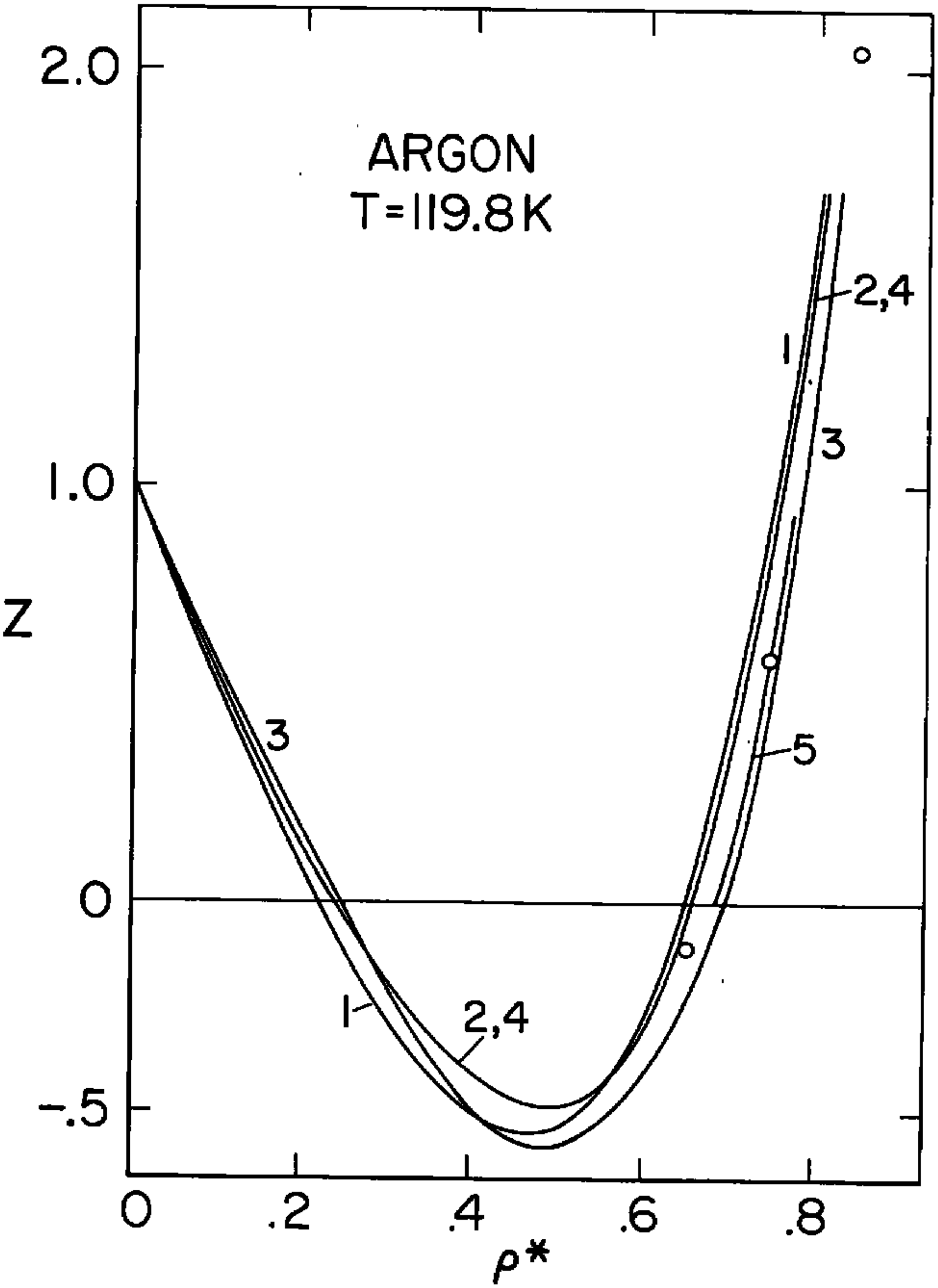

FIG. 4. COMPRESSIBILITY FACTOR FOR ARGON VS REDUCED DENSITY $\rho(N\sigma^3) \equiv \rho^*$ FOR T = 119.8K. CURVES 1, THIS WORK; CURVES 2 AND 4, ZBH THEORY FROM REFERENCES 22 AND 25, RESPECTIVELY; CURVES 3, ZBH THEORY BASED ON MONTE CARLO CALCULATIONS OF PERTURBATION TERMS[24]; CURVES 5, PVT EXPERIMENTAL DATA[33]. THE "COMPUTER EXPERIMENTS"[34] ARE DESIGNATED BY CIRCLES, MONTE CARLO; AND SQUARES, MOLECULAR DYNAMICS.

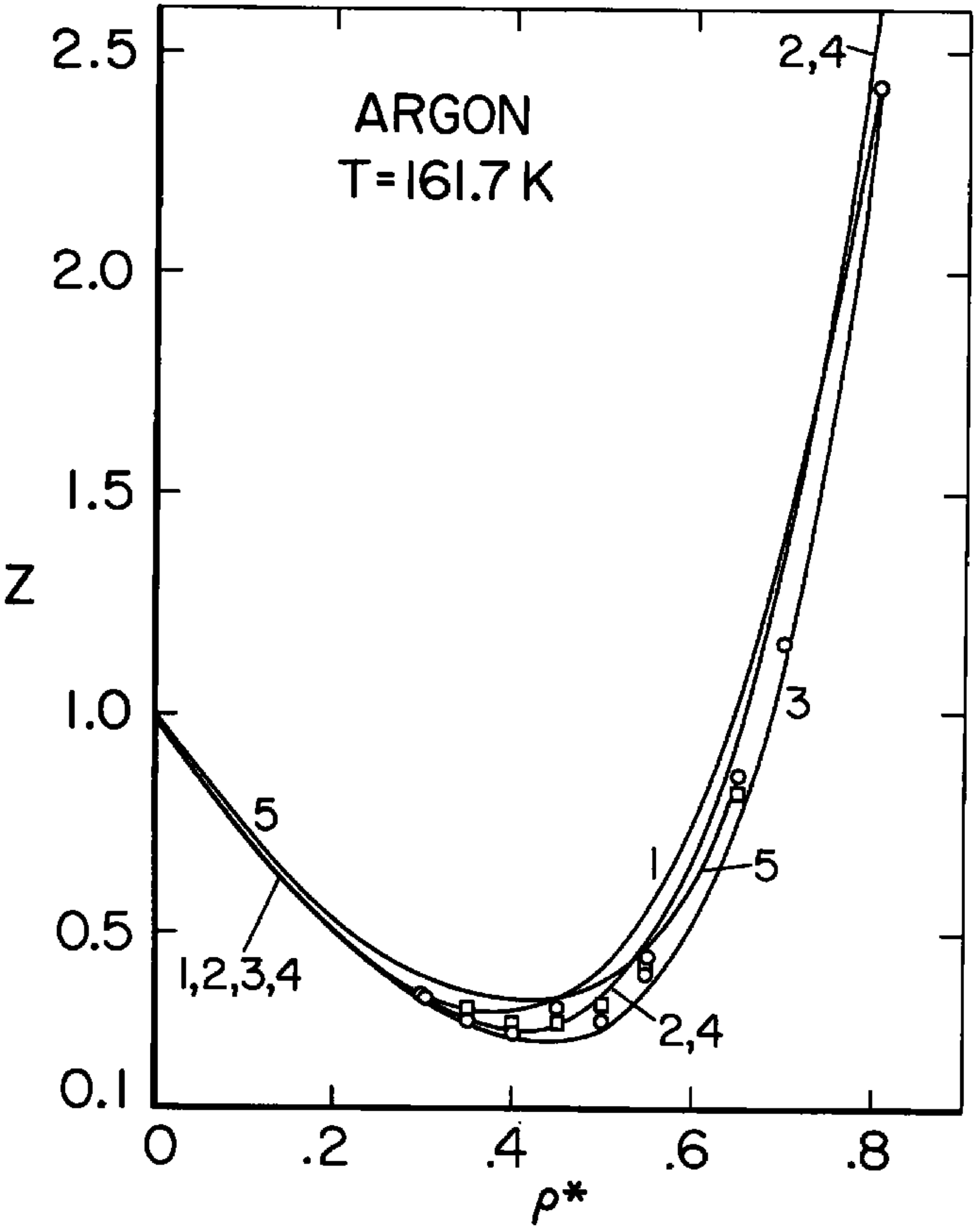

FIG. 5. COMPRESSIBILITY FACTOR VS DENSITY FOR ARGON FOR T = 161.7K; SEE CAPTION, FIG. 4.

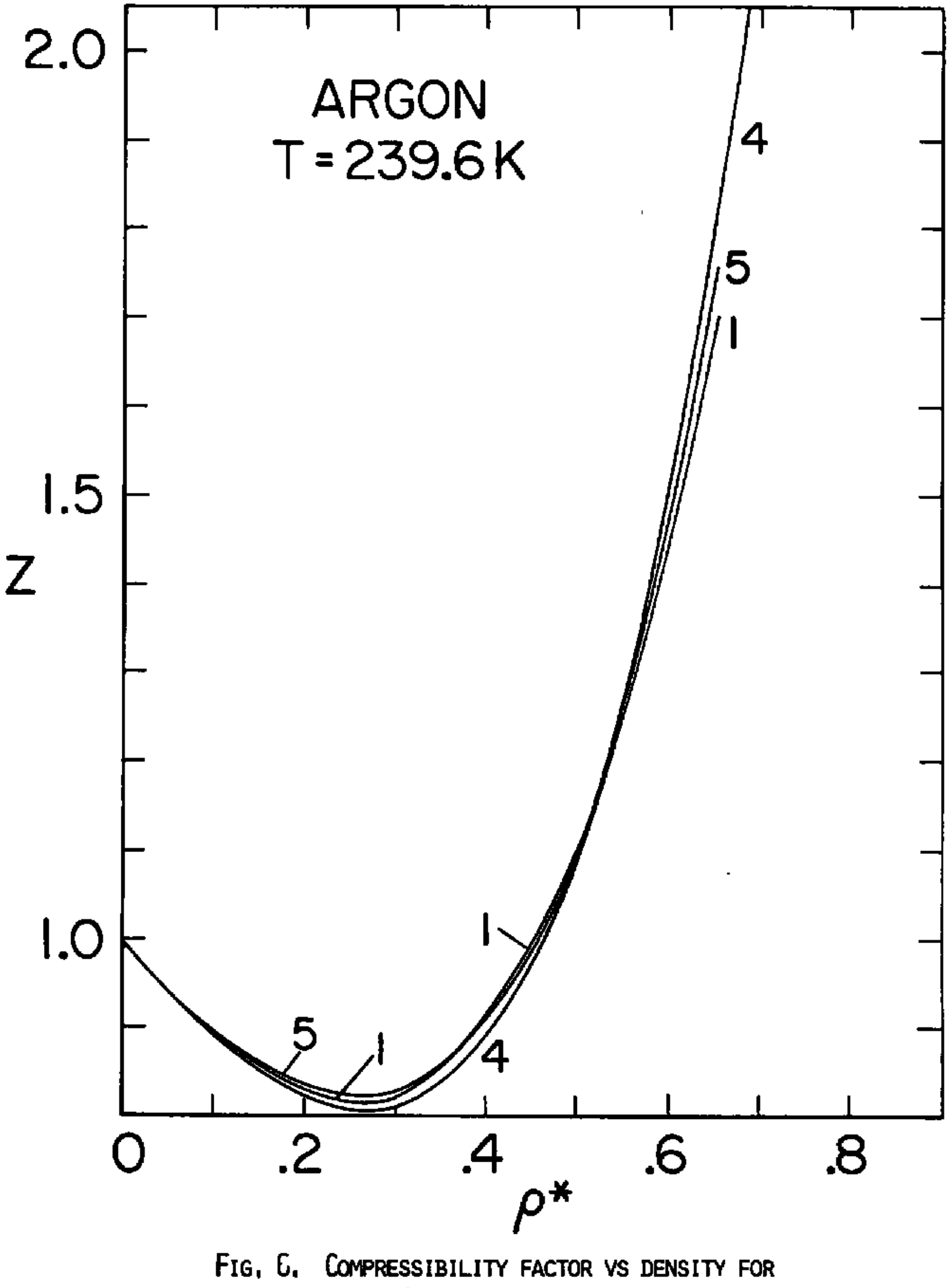

FIG. 6. COMPRESSIBILITY FACTOR VS DENSITY FOR ARGON FOR T = 239.6K; SEE CAPTION, FIG. 4.

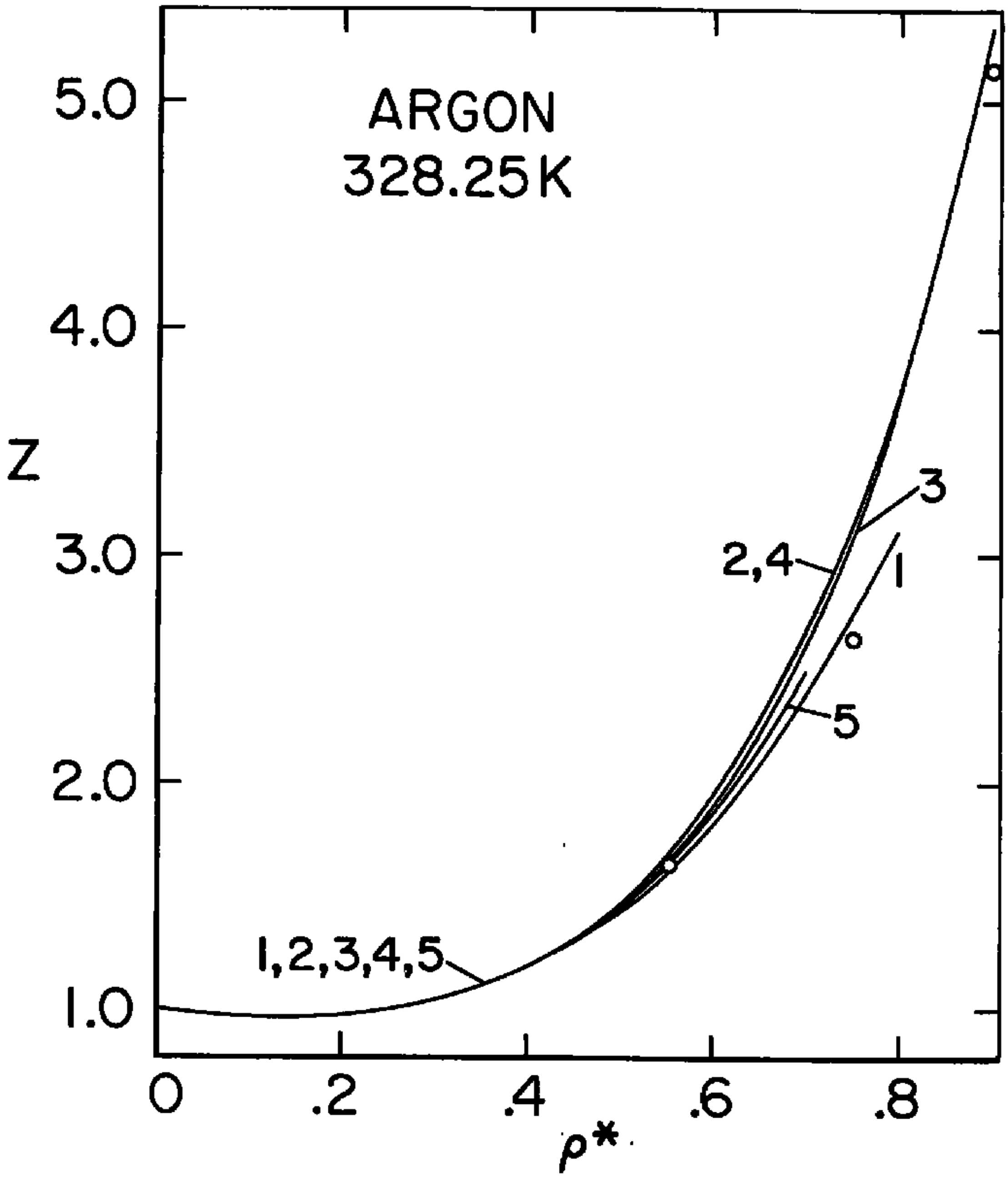

Fig. 7. Compressibility factor vs density for argon for T = 328.25K; see caption, Fig. 4.

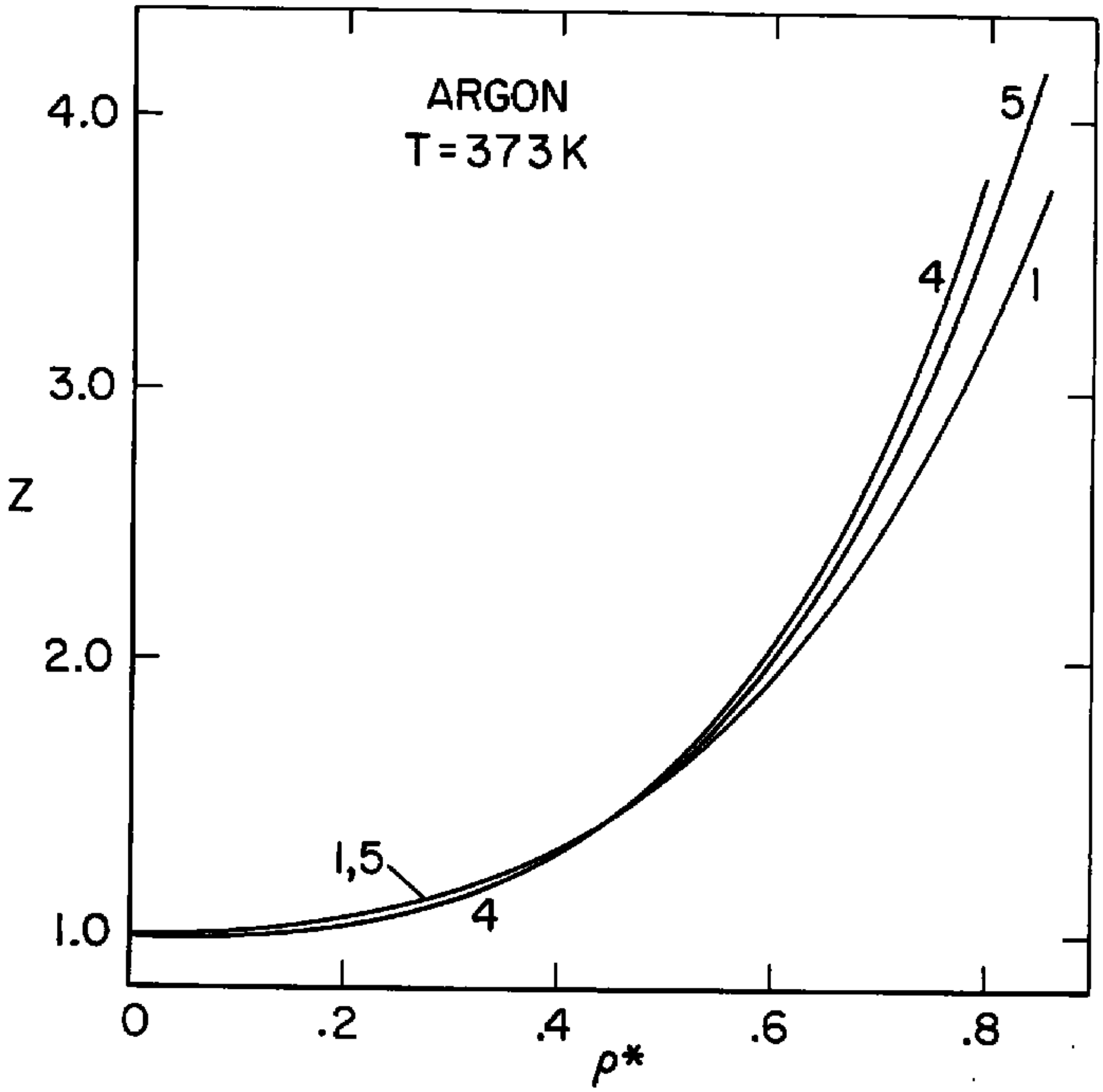

FIG. 8. COMPRESSIBILITY FACTOR VS DENSITY FOR ARGON FOR T = 373K; SEE CAPTION, FIG. 4.

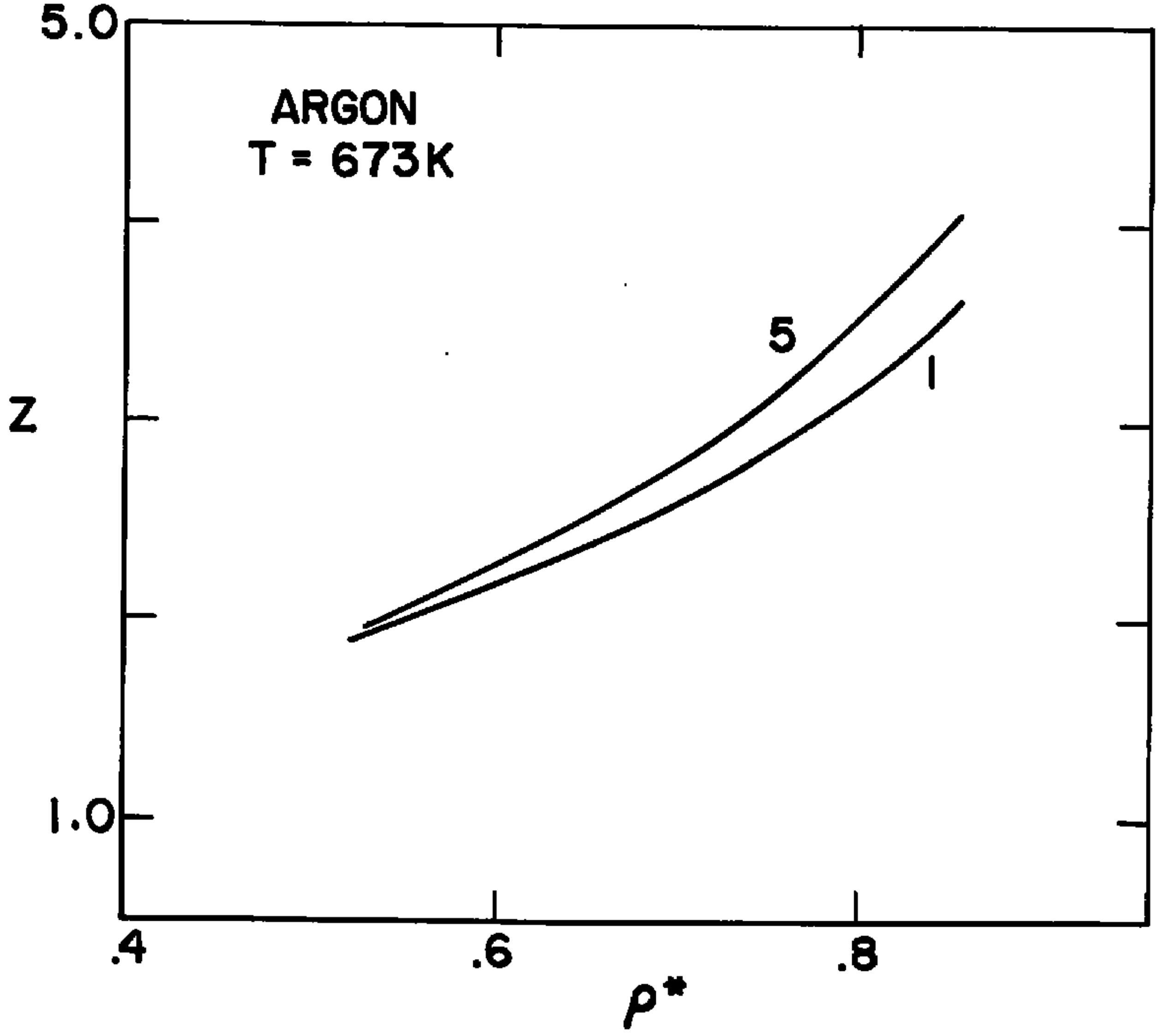

FIG. 9. COMPRESSIBILITY FACTOR VS DENSITY FOR ARGON FOR T = 673K; SEE CAPTION, FIG. 4.

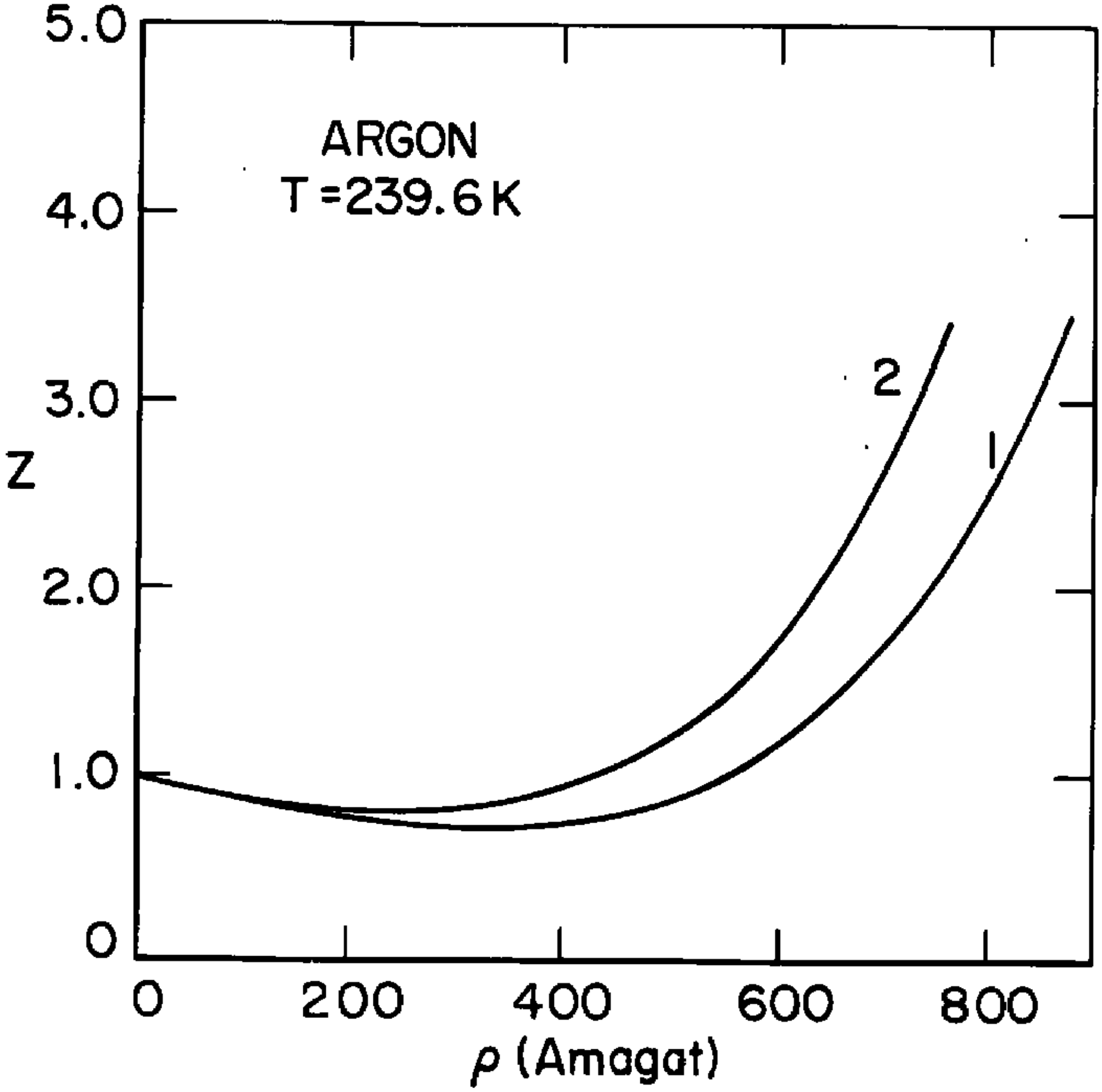

FIG. 10. SENSITIVITY OF EQUATION OF STATE FOR ZBH THEORY TO CHOICE OF POTENTIAL FUNCTION. COMPRESSIBILITY FACTOR IS PLOTTED VS DENSITY IN AMAGAT. FOR CURVE 1, THE REFERENCE POTENTIAL IS THE LENNARD-JONES (18,6); FOR CURVE 2, THE LENNARD-JONES (12,6). THE NUMERICAL RESULTS ARE FROM CALCULATIONS FURNISHED BY TOXVAERD[23] USING POTENTIAL PARAMETERS $\varepsilon/k = 119.8$, $\sigma = 3.405$ FOR THE LATTER AND EQUATION (12) FOR THE FORMER.

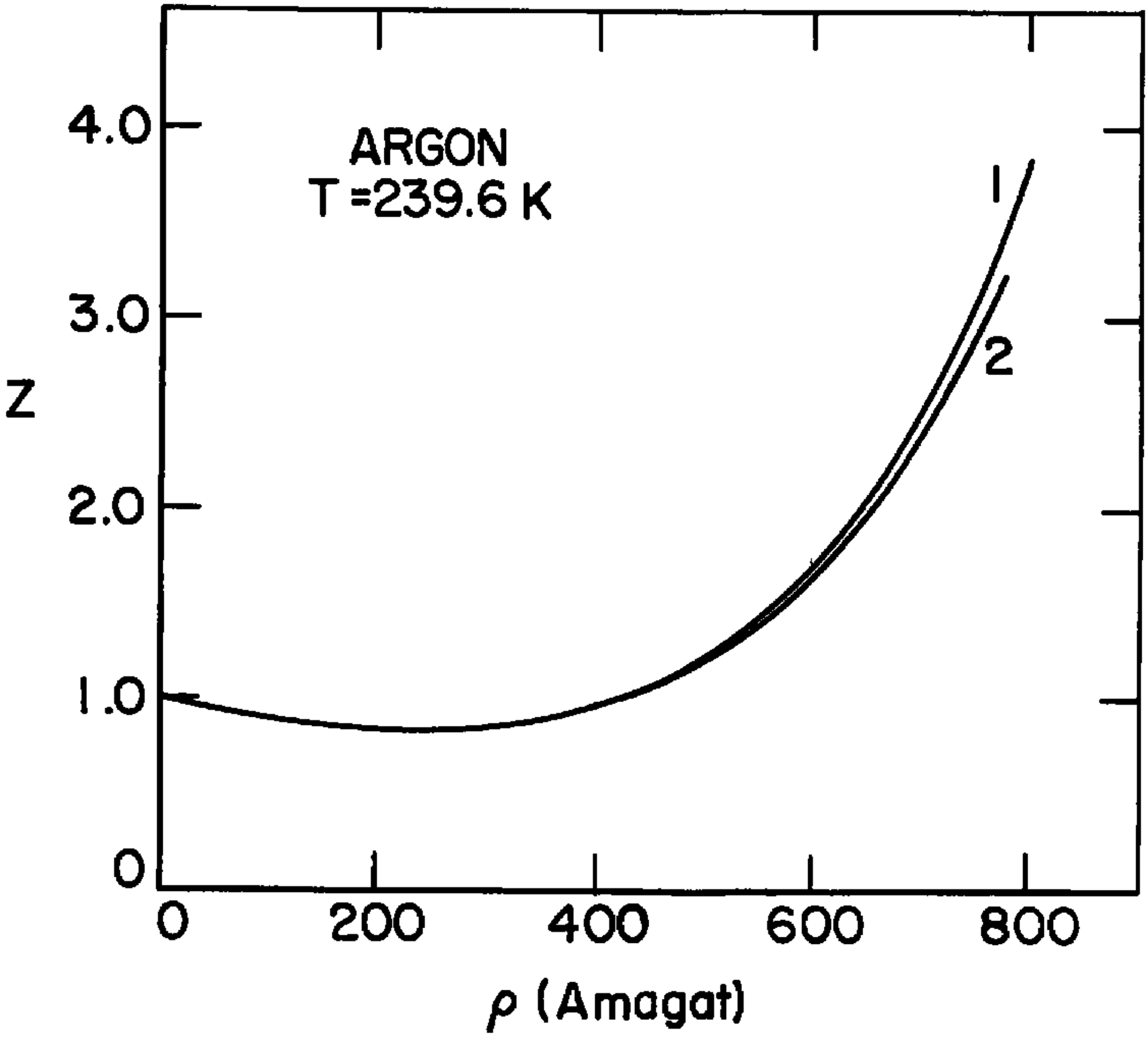

FIG. 11. SENSITIVITY OF PRESENT THEORY TO CHOICE OF POTENTIAL FUNCTIONS. POTENTIAL FUNCTIONS ARE AS DESCRIBED IN CAPTION FOR FIG. 10. THE SMALL DIFFERENCE BETWEEN CURVES 1 AND 2 IS MOSTLY DUE TO THE SLIGHT DIFFERENCES IN SECOND VIRIALS PRODUCED BY THE TWO POTENTIALS IN THE VICINITY OF THE ISOTHERM.

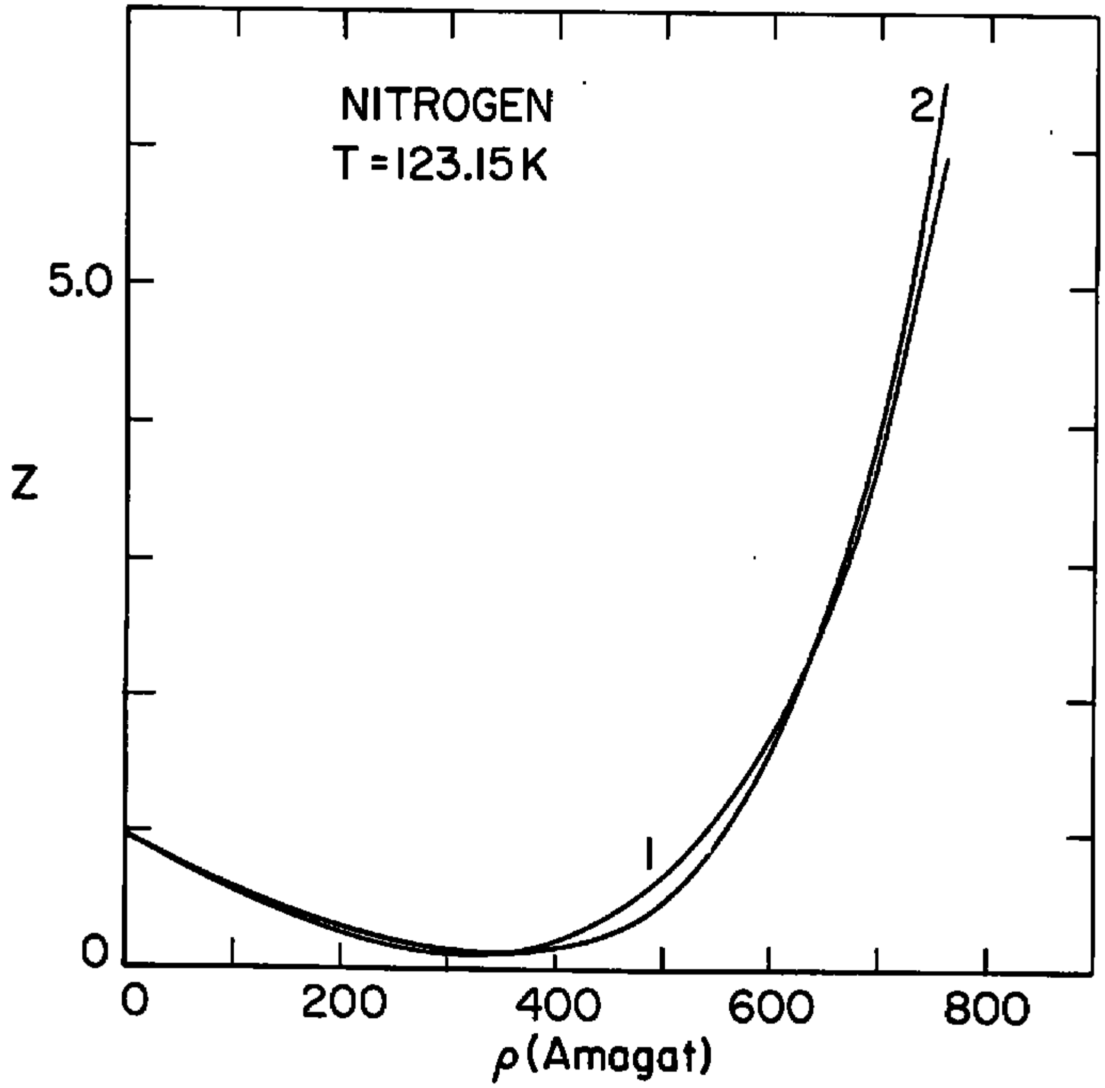

Fig. 12. Compressibility factor vs density in amagat for nitrogen T = 123.15K. Curves 1, present theory; Curves 2, experimental PVT measurements.[55]

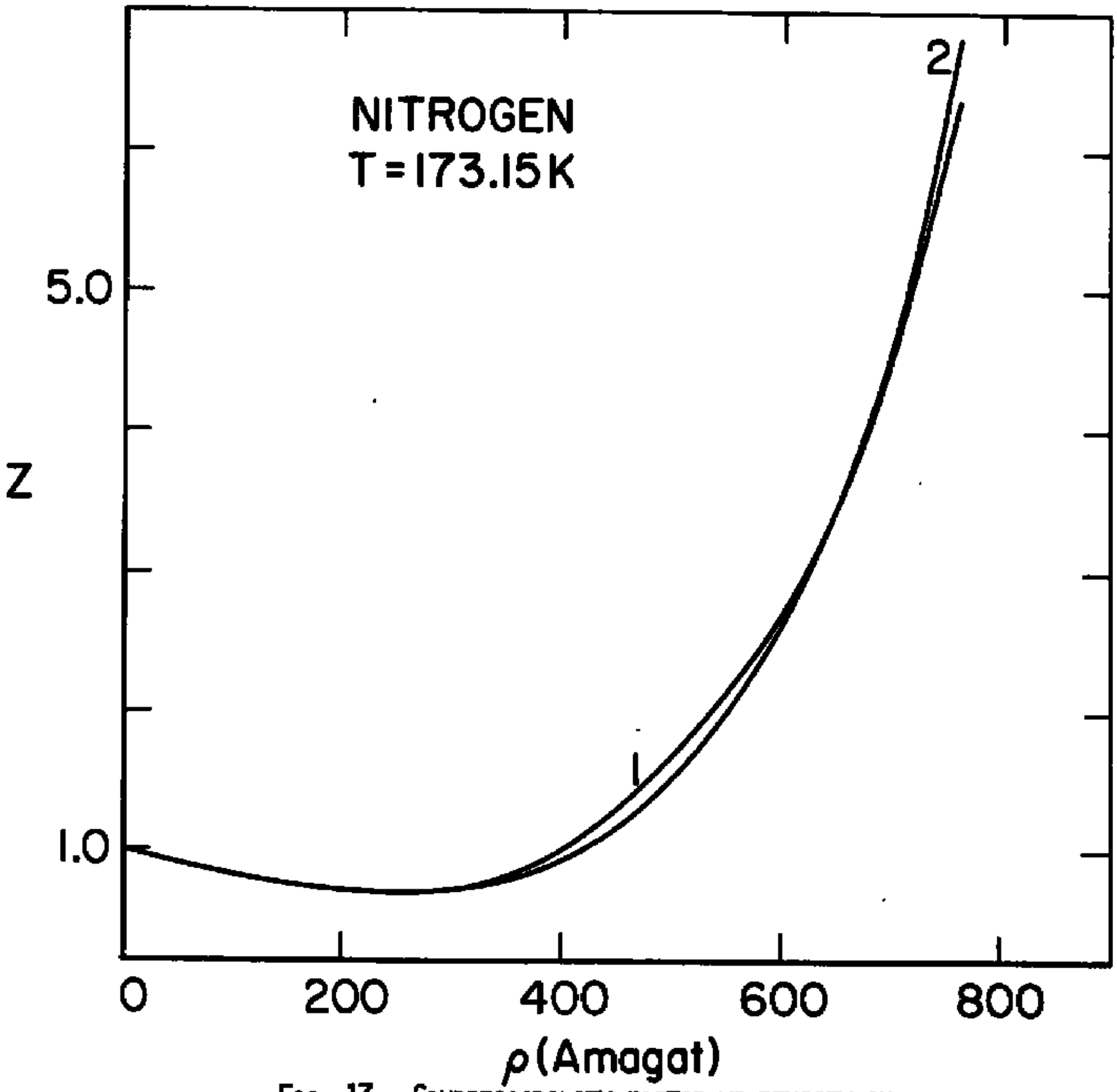

FIG. 13. COMPRESSIBILITY FACTOR VS DENSITY IN AMAGAT FOR NITROGEN T = 173.15K; SEE CAPTION, FIG. 12.

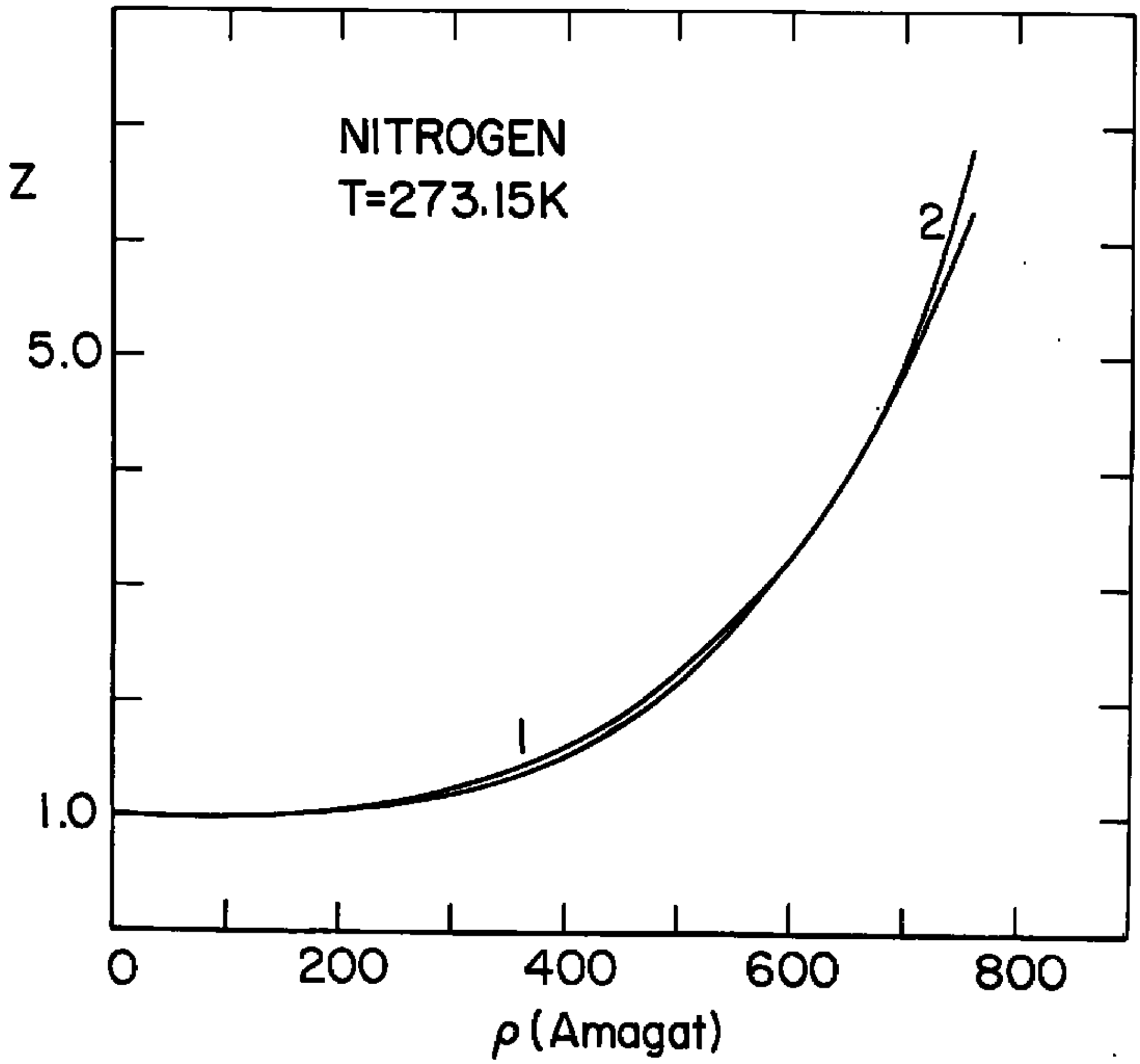

Fig. 14. Compressibility factor vs density in amagat for nitrogen T = 273.15K; see caption, Fig. 12.

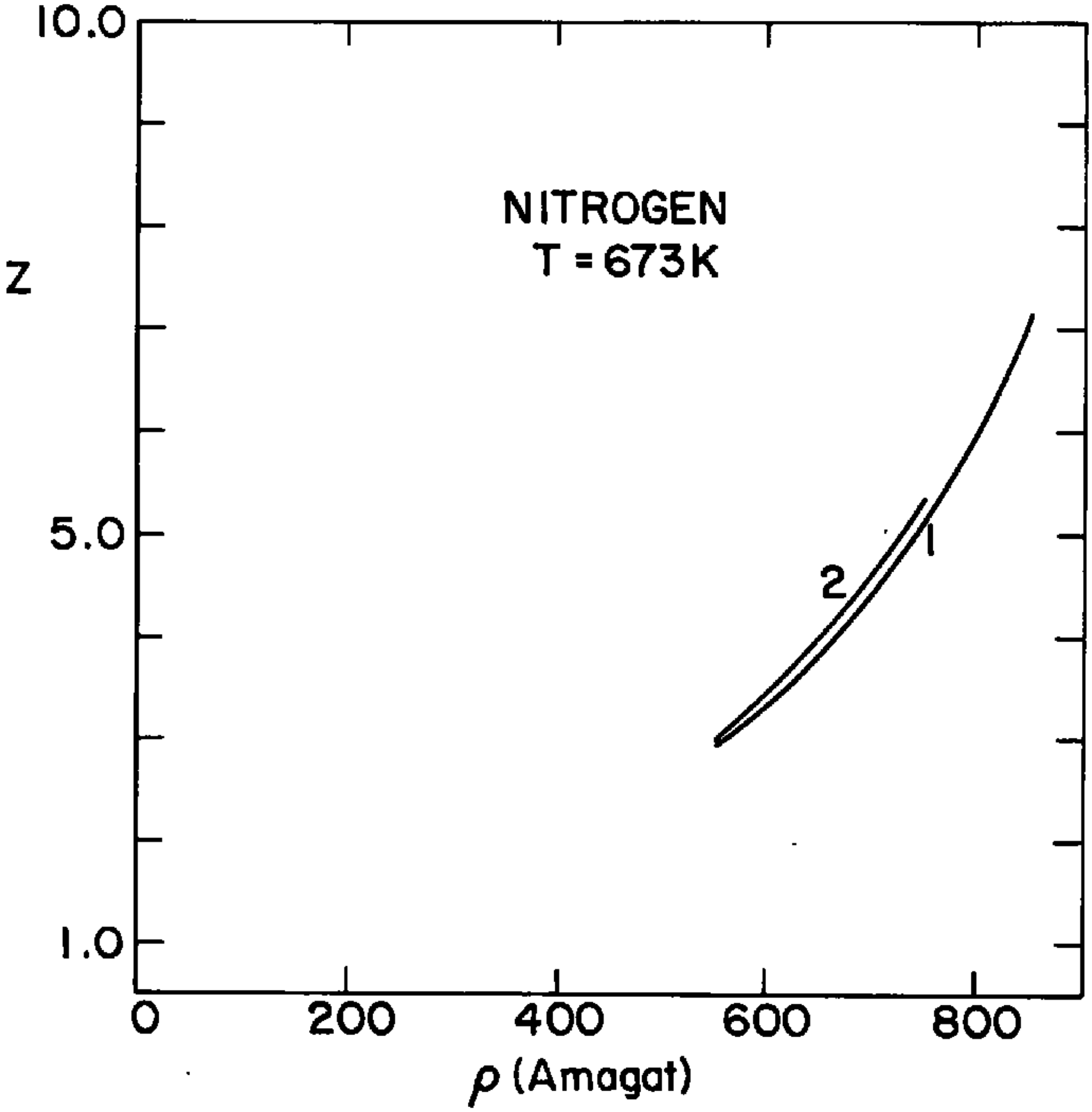

FIG. 15. COMPRESSIBILITY FACTOR VS DENSITY IN AMAGAT FOR NITROGEN T = 673K; SEE CAPTION, FIG. 12.

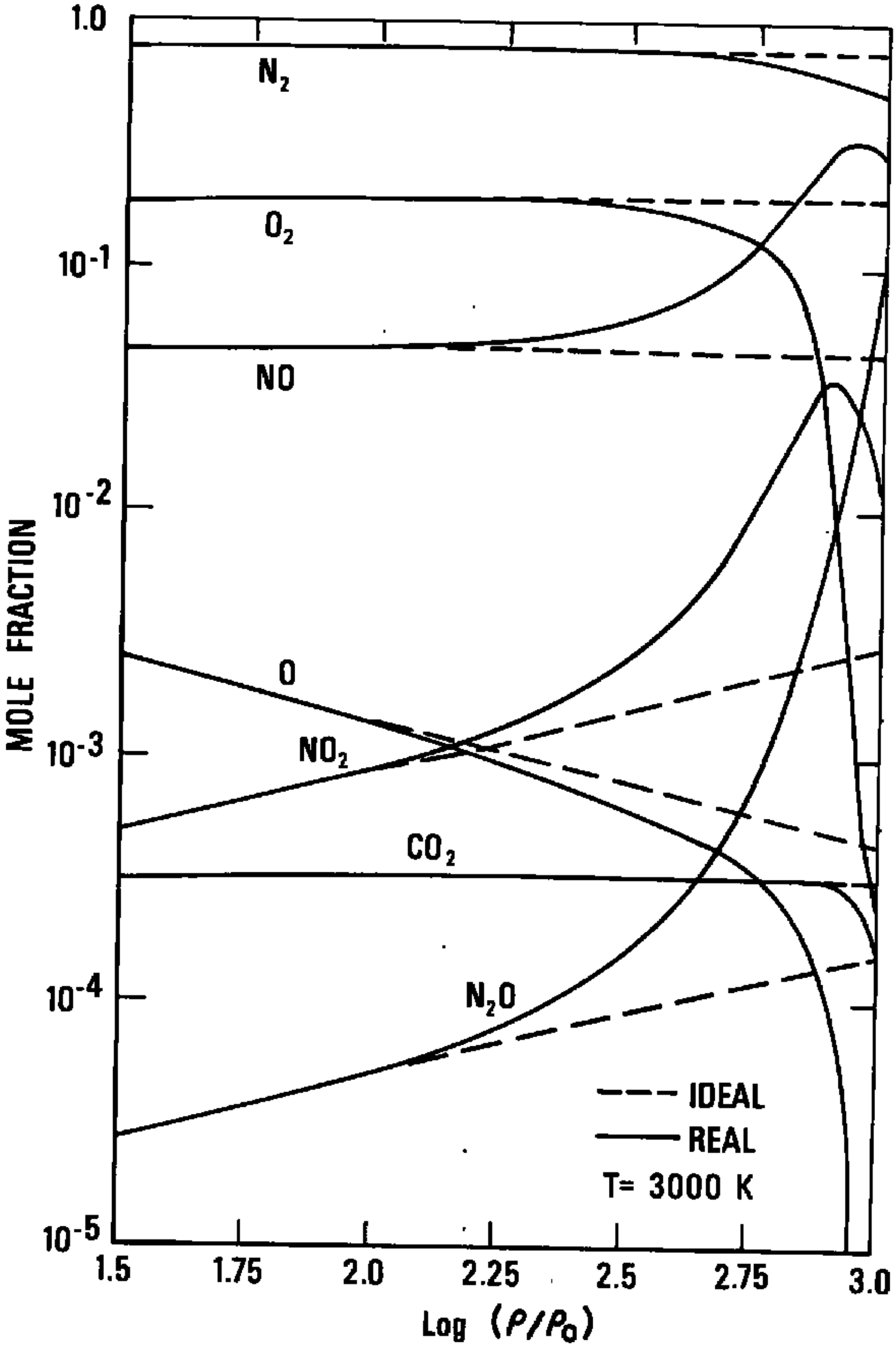

Fig. 16. Concentration versus density for several important species for T = 3000K.

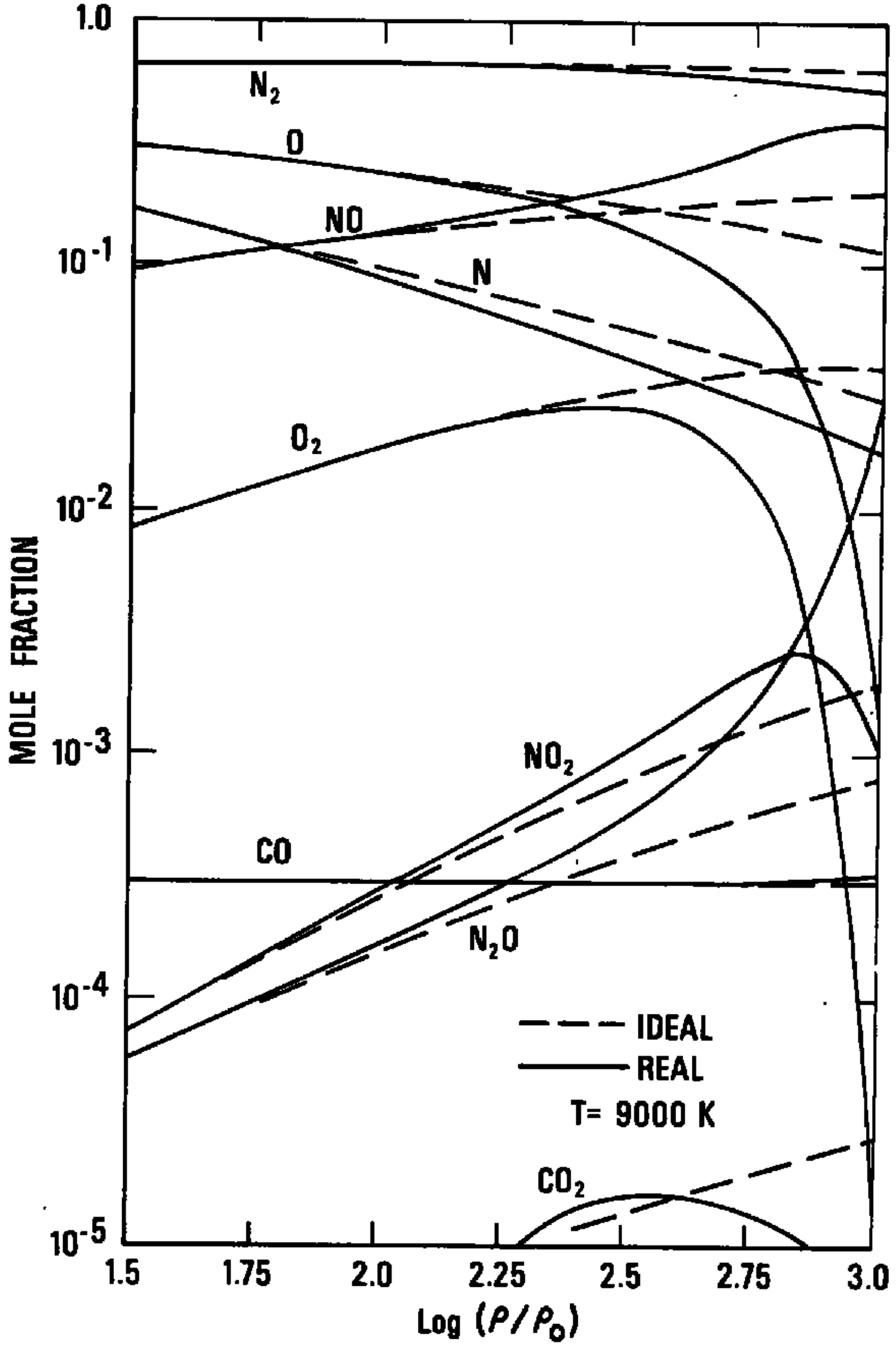

FIG. 17. CONCENTRATION VERSUS DENSITY FOR SEVERAL IMPORTANT SPECIES FOR T = 9000K.